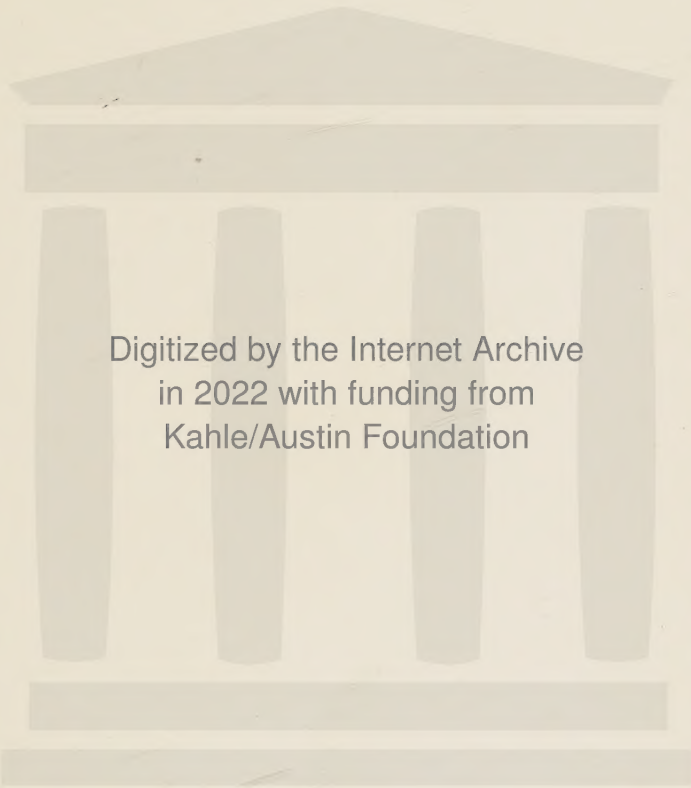


A New View of the Origin
of
Dalton's Atomic Theory





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John Dalton.

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A New View of the Origin
of
Dalton's Atomic Theory

A Contribution to Chemical History

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TOGETHER WITH LETTERS AND DOCUMENTS CONCERNING
THE LIFE AND LABOURS OF JOHN DALTON, NOW FOR
THE FIRST TIME PUBLISHED FROM MANUSCRIPT
IN THE POSSESSION OF THE LITERARY
AND PHILOSOPHICAL SOCIETY
OF MANCHESTER

BY

HENRY E. ROSCOE AND ARTHUR HARDEN

London

MACMILLAN AND CO.

AND NEW YORK

1896

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Introduction

It may seem remarkable that, after the lapse of nearly a century since John Dalton first applied the atomic theory of matter to chemical phenomena, it should be possible to find anything new respecting the genesis of his ideas. And this is the more remarkable when we remember that the life and scientific labours of the great Manchester chemist have formed the subject of independent memoirs at the hands of two such able contemporaries as Charles Henry and Angus Smith. The explanation is to be found in the unlooked-for discovery, in the rooms of the Literary and Philosophical Society of Manchester, where the whole of Dalton's experimental work was carried out, of his laboratory and lecture notebooks contained in a number of manuscript volumes. A careful study of these has led us to conclusions concerning the origin of the atomic theory of chemistry which differ widely from those which have been generally accepted. It has hitherto been supposed that it was the experimental discovery of the law of com-

bination in multiple proportions which led Dalton, seeking for an explanation of this most remarkable fact, to the idea that chemical combination consists in the approximation of atoms of definite and characteristic weight, the atomic theory being thus adopted to explain the facts ascertained by chemical analysis. This prevailing view is found on examination to rest upon the authority of contemporary chemists rather than on any explicit statement on the part of the author himself; for, strange as it may appear, no attempt to explain the genesis of his ideas is to be found in any of Dalton's published writings. Among these newly-discovered manuscript notes, which have hitherto escaped the attention of his biographers, we have found an account in Dalton's own handwriting of this very subject. It is of course well known that he was an ardent adherent of the Newtonian doctrine of the atomic constitution of matter, and that he was thus led to that realistic conception of the structure of gases, which forms so characteristic a feature of his speculations. It now appears that it was from this physical standpoint that Dalton approached the atomic theory, and that he arrived at the idea that the atoms of different substances have different weights from purely physical considerations. This at once led him to conceive of chemical combination as taking place between varying numbers of atoms of definite weight, a position which he then succeeded in confirming

by the results of analyses made both by other chemists and by himself.

The actual relations are, therefore, precisely the inverse of those which are usually accepted. It was the theory of the existence of atoms of different weights which led Dalton to the discovery of the facts of combination in multiple proportions.

The first portion of this work contains a detailed account of the evidence upon which the above conclusion is founded. This is followed by a short epitome of Dalton's daily laboratory notes from 1802 up to the publication of the first part of the *New System of Chemical Philosophy* in 1808, showing the line of thought and of experimental work which he followed during the period when the atomic theory was being elaborated. Next will be found a discussion of the successive and varying series of numbers given by Dalton as representing the atomic weights of the elements, showing how far these were derived from the analyses of others and how far from his own work. The notes for his lectures, delivered at various times and places, have also been reproduced in full, together with a collection of hitherto unpublished letters, which serve to indicate the great reputation which he enjoyed among his contemporaries.

Our thanks are due to the Council of the Literary and Philosophical Society of Manchester for the readiness with which they granted access to the manuscripts in their possession.

CHAPTER I

ON THE GENESIS OF DALTON'S ATOMIC THEORY

THE first published indications of Dalton's atomic theory are, as is well known, appended to a paper "On the absorption of Gases by Water and other Liquids" read before a select audience of nine members and friends in the rooms of the Literary and Philosophical Society of Manchester on 21st October 1803, and printed in the *Manchester Memoirs* with the date of November 1805.

In the concluding paragraph of this paper, Dalton remarks :—"The greatest difficulty attending the mechanical hypothesis, arises from the different gases observing different laws. Why does water not admit its bulk of every kind of gas alike? This question I have duly considered, and though I am not able yet to satisfy myself completely, I am nearly persuaded that the circumstance depends upon the weight and number of the ultimate particles of the several gases: Those whose particles are lightest and single being least absorbable, and the others more according as they increase in

weight and complexity. An enquiry into the relative weights of the ultimate particles of bodies is a subject, as far as I know, entirely new : I have lately been prosecuting this enquiry with remarkable success. The principle cannot be entered upon in this paper ; but I shall just subjoin the results, as far as they appear to be ascertained by my experiments.

“TABLE of the relative weights of the ultimate particles of gaseous and other bodies.

Hydrogen	.	.	.	.	1
Azot	.	.	.	.	4.2
Carbone	.	.	.	.	4.3
Ammonia	.	.	.	.	5.2
Oxygen	.	.	.	.	5.5
Water	.	.	.	.	6.5
Phosphorus	.	.	.	.	7.2
Phosphuretted hydrogen	.	.	.	.	8.2
Nitrous gas	.	.	.	.	9.3
Ether	.	.	.	.	9.6
Gaseous oxide of carbone	.	.	.	.	9.8
Nitrous oxide	.	.	.	.	13.7
Sulphur	.	.	.	.	14.4
Nitric acid	.	.	.	.	15.2
Sulphuretted hydrogen	.	.	.	.	15.4
Carbonic acid	.	.	.	.	15.3
Alcohol	.	.	.	.	15.1
Sulphureous acid	.	.	.	.	19.9
Sulphuric acid	.	.	.	.	25.4
Carburetted hydrogen from stagnant water	.	.	.	.	6.3
Olefiant gas	.	.	.	.	5.3”

An outline of the new theory was included in the course of lectures which Dalton delivered at

the Royal Institution in London during December 1803 and January 1804, and at Edinburgh in 1807, but the general public first became acquainted with it through the medium of a short account which appeared in Dr. Thomas Thomson's *System of Chemistry*, pp. 424-451 of vol. iii. of the third edition, published in 1807. Dalton himself afterwards published a detailed account of the theory, accompanied by another and more extended table of atomic weights in the first part of his *New System of Chemical Philosophy* (Manchester, 1808), of which it forms the third chapter, entitled "On Chemical Synthesis." The second part of the first volume of this work, published in 1810, contained the application of the theory to the chemistry of the elements and the compounds of two elements, as well as a "New Table of the relative weights of atoms" (pp. 352-353).

The first published table of weights is of such a character as to show that its author clearly recognised the facts generally expressed in the laws of combination in definite and multiple proportions. This is seen very distinctly in the cases of the two carburets of hydrogen, and the oxides of sulphur, of carbon, and of nitrogen. The numbers given for nitrous gas and nitrous oxide are obviously misprints for 9.7 and 13.9.

Much interest attaches to the question whether Dalton was led to this mode of interpreting the

facts by the results of his analytical experiments, or whether it was the corpuscular theory of the constitution of matter which induced him to draw theoretical conclusions as to the nature of chemical combination, which he afterwards found were in accordance with fact. In other words, was the atomic theory founded on an experimental knowledge of the law of combination in multiple proportions, or did Dalton arrive at this law as a necessary consequence of the atomic structure of matter?

The evidence to be gathered on this point from the various biographers of the great Manchester chemist and from the historians of chemical science is unsatisfactory, and rather calculated to disturb than settle our minds upon the question.

The most definite evidence is that afforded by Thomson, who spent a day or two with Dalton in August 1804, and carried away with him the very clear and accurate idea of the nature of the new theory published three years later in his *System of Chemistry*. He says:—"Mr. Dalton informed me that the atomic theory first occurred to him during his investigations of olefiant gas and carburetted hydrogen gas, at that time imperfectly understood, and the constitution of which was first fully developed by Mr. Dalton himself. It was obvious from the experiments which he made upon them that the constituents of both were

carbon and hydrogen and nothing else ; he found, further, that if we reckon the carbon in each the same, then carburetted hydrogen contains exactly twice as much hydrogen as olefiant gas does. This determined him to state the ratios of these constituents in numbers, and to consider the olefiant gas a compound of one atom of carbon and one atom of hydrogen ; and carburetted hydrogen of one atom of carbon and two atoms of hydrogen. The idea thus conceived was applied to carbonic oxide, water, ammonia, etc., and numbers representing the atomic weights of oxygen, azote, etc., deduced from the best analytical experiments which chemistry then possessed" (*History of Chemistry*, vol. ii. p. 291).

To this statement Henry, in his *Life of Dalton*, p. 80, appends the following note :—

"In a subsequent biographical account of Dalton, read before the Glasgow Philosophical Society, 5th November 1845, Dr. Thomson repeats the same statement ; but in his notice of Wollaston, read November, 1850, he states :—' Mr. Dalton founded his theory on the analysis of two gases, namely, protoxide and deutoxide of azote. . . . The first of these he considered as a compound of one atom of azote with one atom of oxygen, and the second of one atom of azote united with two atoms of oxygen.' There is no doubt that the earlier statement is the more correct one. For Dalton never regarded nitrous oxide as a ' binary

compound,' but as constituted of two atoms azote and one of oxygen, and nitrous gas as one and one. See all his successive atomic tables, and his letter to Dr. Daubeny. *Atomic Theory*, p. 477."

The account given by Thomson in his *History* has been generally accepted by chemists, and it is usually held to be confirmed by Dalton's own remarks concerning the composition of carburetted hydrogen. In the *New System*, vol. i. p. 444, he says, "No correct notion of the constitution of the gas about to be described¹ seems to have been formed till the atomic theory was introduced and applied in the investigation. It was in the summer of 1804 that I collected, at various times and in various places, the inflammable gas obtained from ponds. . . ."

It now appears, as has been already suggested by Dr. Debus in a *brochure* recently published in German, "On some of the Fundamental Laws of Chemistry,"² that the meaning of this passage is quite the reverse of that which has been attached to it by Henry, Kopp, and other historians of the science. It was, according to this new view, the atomic theory which helped to clear up the existing confusion about the composition of carburetted hydrogen, and not the analysis of the gas which led to the atomic theory.

¹ Marsh gas.

² Cassel. Hofbuchhandlung von Gustav Klaunig, 1894.

Henry adduces further evidence on the question in the shape of two memoranda of conversations held with Dalton, one by his father, the other by himself. The first of these notes is dated 13th February 1830, and is as follows:—"Mr. Dalton has been settled in Manchester thirty-six years. His volume on *Meteorology*, printed but not published before he came here. At p. 132 *et seq.* of that volume, gives distinct anticipations of his views of the separate existence of aqueous vapour from atmospheric air. At that time the theory of chemical solution was almost universally received. These views were the first germs of his atomic theory, because he was necessarily led to consider the gases as constituted of independent atoms. Confirmed the account he before gave me of the origin of his speculations, leading to the doctrine of simple multiples, and of the influence of Richter's table in exciting these views" (Henry, *Life of Dalton*, pp. 62-63). The second conversation is reported in Henry's journal in the following words:—"5th February 1824. The speculations which gave birth to the atomic theory were first suggested to Mr. Dalton by the experiments of Richter on the neutral salts. That chemist ascertained the quantity of any base, as potash for example, which was required to saturate 100 measures of sulphuric acid. He then determined the quantities of the different acids which were adequate to the saturation of the same quantity of

potash. The weights of the other alkaline bases entering into chemical combination with 100 parts of sulphuric acid were then obtained ; and these it is obvious (?) would be equivalent to the saturation of the quantities of the different acids before determined. On these principles a table was formed, exhibiting the proportions of the acids, and the alkaline bases constituting neutral salts. It immediately struck Mr. Dalton that if these saline compounds were constituted of an atom of acid and one of alkali, the tabular numbers would express the relative weights of the ultimate atoms. These views were confirmed and extended by a new discovery of Proust. He maintained that the compounds of iron and oxygen are strictly definite ; in other words, that 100 parts of iron combine either with twenty-eight or forty-two parts of oxygen, but with no intermediate quantity. He did not, however, discover the existence of multiple proportions. This law was first developed by Mr. Dalton, and contributed in a great degree to establish his theory of atomic proportions."

Remarking on the somewhat contradictory nature of the various statements just detailed, Henry (*Life*, p. 85) sums up the evidence very judiciously. "My own belief," he says, "is, that during the three years (1802-1804) in which the main foundations of the atomic theory were laid, Dalton had patiently and maturely reflected on all

the phenomena of chemical combination known to him, from his own researches or those of others, and had grasped in his comprehensive survey, as significant to him of a deeper meaning than to his predecessors, their empirical laws of constant and reciprocal proportion, no less than his own law of multiple proportion, and his own researches in the chemistry of aëriform bodies. On reviewing in conversation, after the lapse of twenty years, the labours of the past, Dalton himself may have failed in recalling the antecedents of his great discovery in the exact order of sequence. His fresh utterances to Dr. Thomson in 1804, when fervently engaged in the investigation, are more likely to be accurate, especially as they are confirmed by the special direction of all his previous researches. At all events it is the obvious duty of a conscientious historian to record faithfully all documents in his possession." In a footnote to this passage he adds : "This view that Dalton's acquaintance with the writings of Richter was posterior, in the order of time, to his experiments on the two carburetted hydrogens and other gases, and that those writings rather confirmed than originally suggested his atomic doctrine, is strengthened by the following decisive words of Dr. Thomson :—I do not know when he adopted these notions, but when I visited him in 1804, at Manchester, he had adopted them ; and at that time both Mr. Dalton himself and myself were ignorant of what had been done by

Richter on the same subject" (*Proc. Phil. Soc. of Glasgow*, 1845-1846, p. 86).

Angus Smith came to very much the same conclusion as Henry:—"From the earliest period of his scientific life," he writes, "Dalton had been accustomed to think carefully on the constitution of the atmosphere; this is seen as early as 1793, in his *Meteorology*. This subject continued to be a favourite one, and led him to gases generally. The experiments quoted at p. 43, on nitrous gas and oxygen, and those mentioned afterwards in a quotation from Dr. Thomson, show the method by which he came to believe, and to prove experimentally, the existence of definite and constant proportion" (*Memoir of Dalton*, p. 231).

Debus, on the other hand, in the pamphlet already referred to "On some of the Fundamental Laws of Chemistry, especially the Dalton-Avogadro Law," has arrived at quite a different conclusion. As mentioned above he interprets Dalton's own remarks about the discovery of the relations between olefiant gas and carburetted hydrogen in a different and certainly a more natural way than had hitherto been done. From the fact that Thomson in his account of the atomic theory (1807) uses the expression *relative density* or *density of the atom* as synonymous with *weight of the atom*, whilst Dalton only uses the latter expression, Debus further argues that when Dalton communicated his theory to Thomson, he must have held the

opinion that these two relations, the relative density and the relative weight of the atoms, were identical, or what Debus appears to consider to be the same thing, that the relative densities of the *gases* were identical with the relative weights of their *atoms*. This view he seeks to confirm by quoting in support of it a passage from the *New System*, p. 188, in which Dalton says: "At the time I formed the theory of mixed gases, I had a confused idea, as many have, I suppose, at this time, that the particles of elastic fluids are all of the same size; that a given volume of oxygenous gas contains just as many particles as the same volume of hydrogenous; or if not, that we had no data from which the question could be solved." On the strength of this argument, which appears to rest on a confusion between the relative density of the *atoms* and the relative density of the *gases* made up of those atoms, between which, by the way, Thomson expressly distinguishes in the case of nitrous gas (NO), Debus concludes (*loc. cit.* 58) that Dalton endeavoured to determine the atomic weights according to the theory laid down in the chapter on "Chemical Synthesis," in order to obtain facts which would either confirm or disprove this law, the law of equal gas volumes. The atomic weights were not proportional to the gas densities, and Dalton, therefore, abandoned the law of equal atomic or molecular volumes for gases. Debus also considers that the passage just quoted

from Dalton entitles him to rank equally with Avogadro as the co-discoverer of what is termed by him throughout the pamphlet in question, "The Dalton-Avogadro Law."

An unexpected light is thrown on these vexed questions by the contents of a number of MS. volumes which have recently been found among the Dalton papers in the possession of the Manchester Literary and Philosophical Society. These comprise, in the first place, an extensive series of laboratory notes, commencing in the year 1802, and going down to Dalton's latest years, containing an almost unbroken record of the experimental work to which he so entirely devoted himself throughout his life, and which supplied him with the materials embodied in his great work, *A New System of Chemical Philosophy*. These notes are bound up in twelve volumes, each of these "compound" volumes being made up of a number of "simple" notebooks of unruled paper, which have been taken out of their original covers and bound together. They have often been commenced at both ends; some of them have been begun, then left unused for a considerable interval, and finally again brought into requisition. Moreover, several of them seem to have been in use at the same time, appropriated to the experiments on different subjects in progress at the moment.

In addition to these very valuable and interesting laboratory records, there is also a notebook

dated 3rd February 1810, in which are contained the notes of the last six lectures of the course of twenty delivered in that year by Dalton at the Royal Institution in London.

The fifteenth and sixteenth lectures deal with heat, but the next one, delivered on 27th January 1810, is of such great interest and importance in connection with the genesis of the atomic theory, that it will be convenient here to quote it in full.

Lecture 17.—CHEMICAL ELEMENTS

“As the ensuing lectures on the subject of *chemical elements* and their combinations will perhaps be thought by many to possess a good deal of novelty, as well as importance, it may be proper to give a brief historical sketch of the train of thought and experience which led me to the conclusions about to be detailed.

Having been long accustomed to make meteorological observations, and to speculate upon the nature and constitution of the atmosphere, it often struck me with wonder how a *compound* atmosphere, or a mixture of two or more elastic fluids, should constitute apparently a homogeneous mass, or one in all mechanical relations agreeing with a simple atmosphere.

Newton had demonstrated clearly, in the 23rd Prop. of Book 2 of the *Principia*, that an elastic fluid is constituted of small particles or atoms of matter, which repel each other by a force increasing in proportion as their distance diminishes. But modern discoveries having ascertained that the atmosphere contains three or more elastic fluids, of different specific gravities, it did not appear to

me how this proposition of Newton would apply to a case of which he, of course, could have no idea.

The same difficulty occurred to Dr. Priestley, who discovered this compound nature of the atmosphere. He could not conceive why the oxygen gas being specifically heaviest, should not form a distinct *stratum* of air at the bottom of the atmosphere, and the azotic gas one at the top of the atmosphere. Some chemists upon the Continent, I believe the French, found a solution of this difficulty (as they apprehended). It was *chemical affinity*. One species of gas was held in solution by the other ; and this compound in its turn dissolved water ; hence *evaporation, rain*, etc. This opinion of air dissolving water had long before been the prevailing one, and naturally paved the way for the reception of that which followed, of one kind of air dissolving another. It was objected that there were no decisive *marks* of chemical union, when one kind of air was mixed with another—the answer was, that the affinity was of a very *slight* kind, not of that energetic cast that is observable in most other cases.

I may add, by the bye, that this is now, or has been till lately, I believe, the prevailing doctrine in most of the chemical schools in Europe.

In order to reconcile or rather adapt this chemical theory of the atmosphere to the Newtonian doctrine of repulsive atoms or particles, I set to work to combine my atoms upon paper. I took an atom of water, another of oxygen, and another of azote, brought them together, and threw around them an atmosphere of heat, as per diagram ; I repeated the operation, but soon found that the watery particles were exhausted (for they make but a small part of the atmosphere). I next combined my atoms of oxygen and azote, one to one ; but I found in

time my oxygen failed ; I then threw all the remaining particles of azote into the mixture, and began to consider how the general equilibrium was to be obtained.

My triple compounds of *water*, *oxygen*, and *azote* were wonderfully inclined, by their superior gravity, to descend and take the lowest place ; the double compounds of *oxygen* and *azote* affected to take a middle station ; and the azote was inclined to swim at the top. I remedied this defect by lengthening the wings of my heavy particles, that is, by throwing more heat around them, by means of which I could make them float in any part of the vessel ; but this change unfortunately made the whole mixture of the same specific gravity as azotic gas—this circumstance could not for a moment be tolerated. In short, I was obliged to abandon the hypothesis of the chemical constitution of the atmosphere altogether, as irreconcilable to the phenomena.

There was but one alternative left, namely, to surround every individual particle of *water*, of *oxygen*, and of *azote*, with heat, and to make them respectively centres of repulsion, the same in a *mixed* state as in a *simple* state. This hypothesis was equally pressed with difficulties ; for, still my oxygen would take the lowest place, my azote the next, and my steam would swim upon the top.

In 1801 I hit upon an hypothesis which completely obviated these difficulties.

According to this, we were to suppose that the atoms of one kind did *not* repel the atoms of another kind, but only those of their own kind. This hypothesis most effectually provided for the diffusion of any one gas through another, whatever might be their specific gravities, and perfectly reconciled any mixture of gases to the Newtonian theorem. Every atom of both or all the gases

in the mixture was the centre of repulsion to the proximate particles of its own kind, disregarding those of the other kind. All the gases united their efforts in counteracting the pressure of the atmosphere, or any other pressure that might be opposed to them.

This hypothesis, however beautiful might be its application, had some improbable features.

We were to suppose as many distinct *kinds* of repulsive powers, as of gases; and, moreover, to suppose that *heat* was not the repulsive power in any one case; positions certainly not very probable. Besides, I found from a train of experiments, which have been published in the *Manchester Memoirs*, that the diffusion of gases through each other was a *slow* process, and appeared to be a work of considerable effort.

Upon reconsidering this subject, it occurred to me that I had never contemplated the effect of *difference of size* in the particles of elastic fluids. By *size* I mean the hard particle at the centre and the atmosphere of heat taken together. If, for instance, there be not exactly the same *number* of atoms of oxygen in a given volume of air, as of azote in the same volume, then the *sizes* of the particles of oxygen must be different from those of azote. And if the *sizes* be different, then on the supposition that the repulsive power is heat, no equilibrium can be established by particles of unequal sizes pressing against each other. (See Diagram.)¹

This idea occurred to me in 1805. I soon found that the *sizes* of the particles of elastic fluids *must* be different. For a measure of azotic gas and one of oxygen, if chemically united, would make nearly *two* measures of nitrous gas, and those *two* could not have

¹ The diagrams here referred to are not reproduced in the notes.

more atoms of nitrous gas than the *one* measure had of azote or oxygen. (See Diagram.) Hence the suggestion that all gases of different kinds have a difference in the *size* of their atoms; and thus we arrive at the reason for that diffusion of every gas through every other gas, without calling in any other repulsive power than the well-known one of *heat*.

This then is the present view which I have of the constitution of a mixture of elastic fluids.

The different *sizes* of the particles of elastic fluids under like circumstances of temperature and pressure being once established, it became an object to determine the relative *sizes* and *weights*, together with the relative *number* of atoms in a given volume. This led the way to the combinations of gases, and to the *number* of atoms entering into such combinations, the particulars of which will be detailed more at large in the sequel. Other bodies besides elastic fluids, namely liquids and solids, were subject to investigation, in consequence of their combining with elastic fluids. Thus a train of investigation was laid for determining the *number* and *weight* of all chemical elementary principles which enter into any sort of combination one with another.

1. Divisibility of matter considered. Atoms—see Newton's ideas.

2. Elastic fluids exhibit matter in extreme division. Newton, B. 2; Prop. 23. See Diagram.

Hydrogen and oxygen cannot be broken down into finer kinds by electricity. Like flour, etc.; sugar, etc.

Compound gases, as nitrous, carbonic acid, are separated into their ulterior elements by electricity. . . . See Diagram atmosphere.

3. Other bodies constituted of atoms as well as elastic fluids — charcoal, sulphur, phosphorus. Metals by combining with atoms of elastic fluids show that they have atoms.
4. All atoms *of the same kind* alike in wt. bulk.
5. Atoms of different kinds unequal in wt., etc.
See Newton, 2.
6. Bodies deemed simple till they are decomposed.
7. Chemical synthesis. Exhibit two particles. See also Newton, 3.
8. Table of arbitrary marks.
Gay-Lussac's notion."

The operation of combining the atoms upon paper as described in these notes is a little difficult to follow. Only the proportion of the constituents of the atmosphere by weight and volume being known, some theory as to the relative number of particles was necessary before Dalton could write : "I soon found that the watery particles were exhausted."

No doubt at this time he still entertained the "confused idea," to which he confesses in the *New System*, p. 188, "that the particles of elastic fluids are all of the same size ; that a given volume of oxygenous gas contains just as many particles as the same volume of hydrogenous," and he, therefore, made the number of particles of each constituent directly proportional to its pressure in the atmosphere. He thus, of course, found (the necessity for a trial on paper being, indeed, hardly obvious)

that after using all the water particles to form triple compounds with an atom of nitrogen and one of oxygen, the number of nitrogen atoms left was far too large to simply provide a companion atom for each one of oxygen, and he was, therefore, left with a surplus of nitrogen atoms on hand, which were of course free.

It may be well to remember that, according to Dalton's view, which is a modification of that of Newton and Lavoisier, each atom or particle of a gas consisted of an exceedingly small central nucleus of solid matter surrounded by an enormously more bulky elastic atmosphere of heat, of great density next the atom, but gradually growing rarer according to some power of the distance. To this atmosphere of heat was ascribed the power of repulsion by means of which the elastic state of the gas was maintained. By increasing the amount of heat round each atom the density of the gas would, therefore, be diminished.

In Dalton's paper atmosphere, however, the lightest particles were those of unaltered nitrogen, with which Dalton evidently felt a delicacy in interfering; he, therefore, had no alternative but, as he says, "to make the whole mixture of the same specific gravity as azotic gas, a state of things which could not be for a moment tolerated." Precisely the same difficulties assailed him when he imagined the atmosphere as a simple mixture of repulsive atoms of nitrogen, oxygen, and water;

there was apparently nothing to prevent the gases from arranging themselves in the order of their specific gravities.

The way in which Dalton surmounted this difficulty by means of his celebrated theory that gases behave as vacua towards one another is sufficiently clear, but the view which finally replaced that theory, and gave the inspiration which led to the atomic theory, may perhaps not be quite so readily understood. The complete account of the idea, as given in the *New System*, pp. 187-191, may, therefore, be helpful on this point :—

“ I shall now proceed to give my present views on the subject of mixed gases, which are somewhat different from what they were when the theory was announced, in consequence of the fresh lights which succeeding experience has diffused. In prosecuting my enquiries into the nature of elastic fluids, I soon perceived it was necessary, if possible, to ascertain whether the atoms or ultimate particles of the different gases are of the same size or volume in like circumstances of temperature and pressure. By the size or volume of an ultimate particle, I mean, in this place, the space it occupies in the state of a pure elastic fluid; in this sense the bulk of the particle signifies the bulk of the supposed impenetrable nucleus, together with that of its surrounding repulsive atmosphere of heat. At the time I formed the theory of mixed gases, I had a confused idea, as many have, I suppose, at this

time, that the particles of elastic fluids are all of the same size ; that a given volume of oxygenous gas contains just as many particles as the same volume of hydrogenous ; or if not, that we had no data from which the question could be solved. But from a train of reasoning, similar to that exhibited at p. 71,¹ I became convinced that different gases have *not* their particles of the same size : and that the following may be adopted as a maxim, till some reason appears to the contrary ; namely,—

“That every species of pure elastic fluid has its particles globular and all of a size ; but that no two species agree in the size of their particles, the pressure and temperature being the same.

“There was another thing concerning which I was dubious ; whether heat was the cause of repulsion. I was rather inclined to ascribe repulsion to a force resembling magnetism, which acts on one kind of matter, and has no effect on another. For, if heat were the cause of repulsion, there seemed no reason why a particle of oxygen should not repel one of hydrogen with the same force as one of its own kind, especially if they were both of a size. Upon more mature consideration, I see no sufficient reason for discarding the common opinion, which ascribes repulsion to heat ; and I think the phenomena of mixed gases may be still

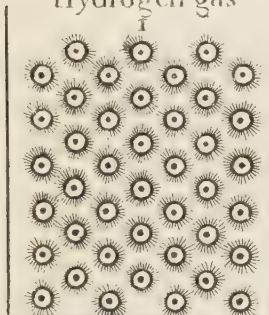
¹ The formation of two volumes of nitrous gas from one of nitrogen and one of oxygen.

accounted for, by repulsion, without the postulatam, that their particles are mutually inelastic, and free from such of the preceding objections as I have left unanswered.

“ When we contemplate upon the disposition of the globular particles in a volume of pure elastic fluid, we perceive it must be analogous to that of a square pile of shot ; the particles must be disposed into horizontal strata, each four particles forming a square : in a superior stratum, each particle rests upon four particles below, the points of its contact with all four being 45° above the horizontal plane, or that plane which passes through the centres of the four particles. On this account the pressure is steady and uniform throughout. But when a measure of one gas is presented to a measure of another in any vessel, we have then a surface of elastic globular particles of one size in contact with an equal surface of particles of another : in such case the points of contact of the heterogeneous particles must vary all the way from 40° to 90° ; an intestine motion must arise from this inequality, and the particles of one kind be propelled amongst those of the other. The same cause which prevented the two elastic surfaces from maintaining an equilibrium, will always subsist, the particles of one kind being from their size unable to apply properly to the other, so that no equilibrium can ever take place amongst the heterogeneous particles. The intestine motion must therefore continue till

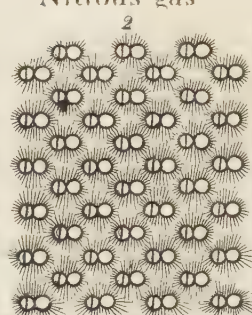
Hydrogen gas

1



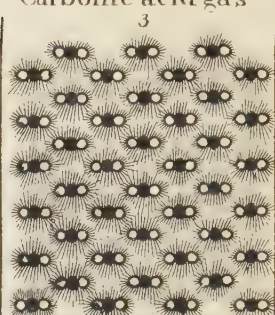
Nitrous gas

2

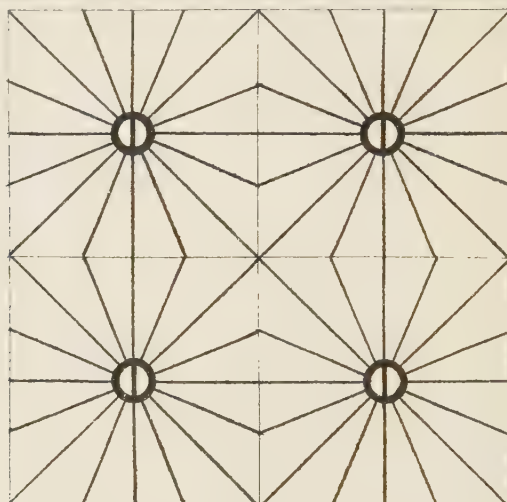


Carbonic acid gas

3

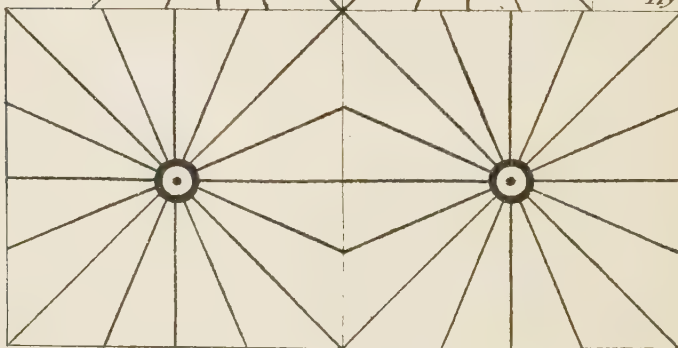


4



Azote

5



Hydrogen

the particles arrive at the opposite surface of the vessel against any point of which they can rest with stability, and the equilibrium at length is acquired when each gas is uniformly diffused through the other. In the open atmosphere no equilibrium can take place in such case till the particles have ascended so far as to be restrained by their own weight; that is, till they constitute a distinct atmosphere."

The idea does not appear to have been very carefully thought out, and although the conditions of equilibrium would certainly be disturbed, it is doubtful whether the intestine motion of which Dalton speaks would have been set up in a vessel filled with his atoms. The point of importance, however, for our purpose is to understand what Dalton thought about the subject, not whether he was justified in so thinking. The theory may be further illustrated by the diagrams (Plates 1 and 2) reproduced from the second part of the *New System*, p. 548, the description of which is as follows:—

"PLATE 7. Figs. 1, 2, and 3 represent profile views of the disposition and arrangement of particles constituting elastic fluids, both simple and compound, but not mixed; it would be difficult to convey an adequate idea of the last case, agreeably to the principles maintained, p. 190. The principle may, however, be elucidated by the succeeding figures.

"Fig. 4 is the representation of four particles

of azote with their elastic atmospheres, marked by rays emanating from the solid central atom ; these rays being exactly alike in all the four particles can meet each other, and maintain an equilibrium.

“ Fig. 5 represents two atoms of hydrogen drawn in due proportion to those of azote, and coming in contact with them ; it is obvious that the atoms of hydrogen can apply one to the other with facility, but can not apply to those of azote, by reason of the rays not meeting each other in like circumstances ; hence, the cause of the intestine motion which takes place on the mixture of elastic fluids, till the exterior particles come to press on something solid.

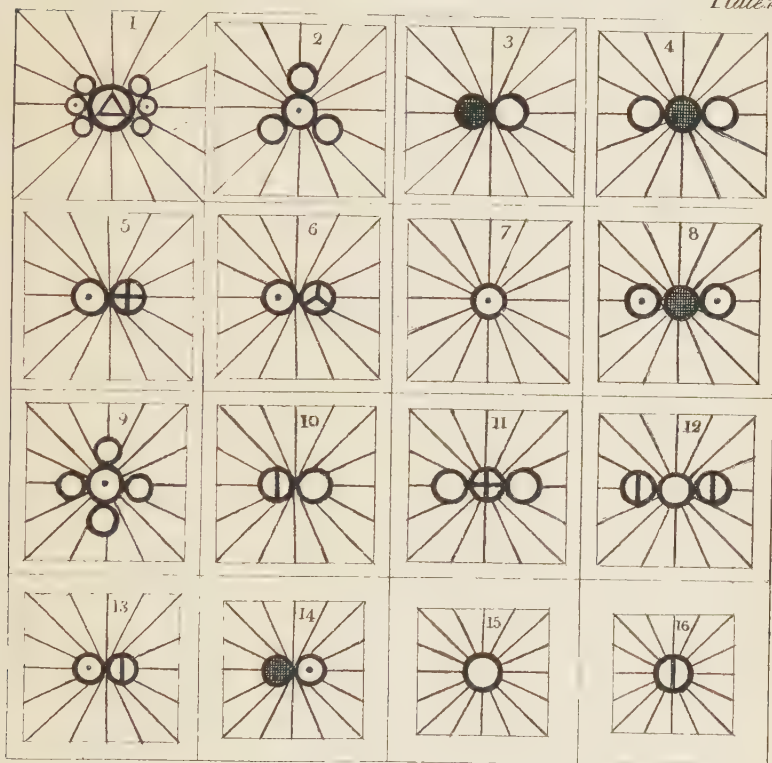
“ PLATE 8. The first sixteen figures represent the atoms of different elastic fluids, drawn in the centres of squares of different magnitude, so as to be proportionate to the diameters of the atoms as they have been herein determined. Fig. 1 is the largest ; and they gradually decrease to Fig. 16, which is the smallest ; namely, as under :—

Fig.		Fig.
1.	Superfluante of silex . . . 1.15	9. Oxymuriatic acid .981
2.	Muriatic acid . . . 1.12	10. Nitrous gas . .980
3.	Carbonic oxide 94	11. Sulphurous acid . .95
4.	Carbonic acid . . . 1.00	12. Nitrous oxide . .947
5.	Sulphuretted hydrogen . 1.00	13. Ammonia . . .909
6.	Phosphuretted hydrogen 1.00	14. Olefiant gas . .81
7.	Hydrogen . . . 1.00	15. Oxygen . . .794
8.	Carburetted hydrogen . 1.00	16. Azote . . .747 ”

The method employed by Dalton in calculating these numbers is a very simple one. The number

DIAMETERS OF ELASTIC ATOMS

Plate 2



of particles in unit volume of a gas is proportional to the weight of that volume, or the density of the gas, divided by the weight of a single particle, its atomic weight. The diameter of a particle is, of course, inversely proportional to the cube root of the number present in a given volume. Taking hydrogen as the standard atomic weight, the diameter of the particle of any gas compared with that of one of hydrogen is therefore given by the expression $d = \sqrt[3]{\frac{w}{s}}$, in which s is the relative density of the gas, and w the relative weight of its ultimate particle.

It may be observed that no less than five out of the sixteen gases tabulated above have their particles of the same diameter, and it does not appear how Dalton reconciled this anomaly with the experimental facts.

As we have seen (p. 16) Dalton states in his lecture notes that the idea that the uniform diffusion of gases might be explained by the different sizes of their constituent atoms occurred to him in 1805, and led to the determination of the relative size, number, and weight of these atoms. This date must be a clerical error for 1803, since he communicated an account of the atomic theory to Thomson in 1804, and, as we shall see, he had worked out a table of the diameters of the atoms in September 1803.

The account of the origin of the atomic theory

here presented to us strikingly confirms the opinion expressed by his sagacious biographer in the passage already quoted (p. 8).

It shows us very clearly how Dalton, starting from the Newtonian doctrine of repulsive atoms or particles, had been brought face to face with the problem of determining the relative size and weight (for, as we have seen, the one involved the other) of these small and almost infinitesimal particles. The method he adopted, and at all events some of his reasons for adopting it, become plain when we refer to the laboratory notes.

One of the small "constituent" notebooks of the first volume (pp. 244-289) was reserved by him for this subject and contains matter of the highest historical interest. The portions of it which bear upon the point under discussion are printed verbatim, and some of the most important of these (*viz.* from pp. 244, 248 and 249) are reproduced in facsimile (Plates 3 and 4) from photographs taken from the original manuscripts.

Vol. I. Page 244

Observations on the ultimate particles of bodies and their combinations.

6th September 1803

Characters of elements—

- Hydrogen.
- ⊙ Oxygen.
- ⊕ Azote.
- Carbone, pure charcoal.
- ⊕ Sulphur.

The characters on this page constitute the very earliest set of atomic symbols with which we are acquainted ; it is interesting to note that the signs for oxygen and hydrogen are not those used in the later tables, but were interchanged (see Plate 3 for facsimile reproduction).

Page 245

N.B.—The ultimate atoms of bodies are those particles which in the gaseous state are surrounded by heat ; or they are the centres or *nuclei* of the several small elastic globular particles.

Page 246

Enquiry into the specific gravity of the ultimate particles or elements.

Though it is probable that the specific gravities (*sic*) of different elastic fluids has some relation to that of their ultimate particles, yet it is certain that they are not the same thing ; for the ult. part. of water or steam are certainly of greater specific gravity than those of oxygen, yet the last gas is *heavier* than steam.

Dalton here, at the very first conception of the atomic theory, touches on the great difficulty which was to prove a stone of offence to so many of his successors. The fact that steam, the ultimate particle of which contains both oxygen and hydrogen, is specifically lighter than oxygen, is proof to him that the specific gravities of gases and the relative weights of their ultimate particles are not identical,

and that, therefore, the diameters of the atoms are not the same for all substances.

Page 247

From the composition of water and ammonia we may deduce ult. at. azot 1 to oxygen 1.42 :—

Ult. atom of nit. gas should therefore weigh 2.42 azot.

Ult. atom of oxygen 1.42 oxygen.

According to this 1 oxygen will want 1.7 nitrous.

Sulph. Oxy.

Chenevix— $61\frac{1}{2} + 38\frac{1}{2} =$ sulphuric A.

Then $61\frac{1}{2} + 19\frac{1}{4}$ should be sulphureous.

This gives ult. part. of sulphur to oxy. 3.2 : 1 nearly.

Sulph. Oxy.

Thenart 56 + 44

56 + 22 sulphureous.

Fourcroy says 85 + 15 = sulphureous.

Page 248

Ult. at. Hydrogen	.	.	.	1
„ Oxygen .	.	.	.	5.66
„ Azot .	.	.	.	4
„ Carbon (charcoal)	.	.	.	4.5
„ Water .	.	.	.	6.66
„ Ammonia .	.	.	.	5
„ Nitrous gas .	.	.	.	9.66
„ Nitrous oxide .	.	.	.	13.66
„ Nitric acid .	.	.	.	15.32
„ Sulphur .	.	.	.	17
„ Sulphureous acid .	.	.	.	22.66
„ Sulphuric acid .	.	.	.	28.32
„ Carbonic Acid .	.	.	.	15.8
„ Oxide of carbone .	.	.	.	10.2

The most important matter with respect to the history of the origin of the atomic theory is to

(244)

Observations

on the ultimate particles of Bodies,
 & their combinations.

Sept. 6 - 1803.

Characters of Elements. —

- Hydrogen
- Oxygen
- ① Azote — pure charcoal.
- Carbon ~~pure or diamond~~
- ⊕ Sulphur

(248)

At. wt.	Hydrogen	1.000
—	Oxygen	8.000
—	Azote	5.66
—	Carbon (Charcoal)	5.00
—	Water	9.00
—	Ammoniac	17.00
—	Nitrous Gas	10.66
—	Nitrous Oxide	13.66
—	Nitric Acid	21.32
—	Sulphur	16.00
—	Sulphurous acid	22.66
—	Sulphuric acid	48.32
—	Carbonic Acid	18.8
—	Oxide of Carbon	12.2

be found on these two pages. Page 248 contains a table of atomic weights (see facsimile reproduction Plate 3) written out on 6th September 1803, two years before the one published in the *Memoirs* (i. 287) in 1805, and about a year before the verbal communication made to Thomson in the summer of 1804, which formed the basis of the account of the atomic theory published in the latter's *System of Chemistry*. In this table it will be seen that the law of combination in multiples is as clearly recognised as in any of the subsequent ones, but no mention whatever is made of carburetted hydrogen, either light or heavy. The experiments on carburetted hydrogen from stagnant water were in fact not made until the summer of 1804, nearly a year after this table of atomic weights had been drawn up, and this date is trebly attested (1) by the statement of Dalton (*New System*, p. 444), (2) by Thomson (*History*, ii. p. 291), and (3) by the evidence of the Notebook, in which the first experiments on this substance are found under date of 6th August 1804.

This disposes once and for all of the opinion commonly held, founded on Thomson's statement, that the atomic theory was suggested by a comparison of the analyses of marsh gas and olefiant gas, and this conclusion is in full agreement with the record already quoted from the lecture notes.

On p. 247, opposite to the table, we find the

clue to the reasoning which had led Dalton to these numbers. The weights of hydrogen, oxygen, and azot, it will be seen, are derived from the composition of water and ammonia (the actual numbers will be afterwards separately discussed), whilst the weight of an atom of sulphur is calculated from an analysis of sulphuric acid by Chenevix. No information is actually given as to the source of the number for carbon, but it appears certain that this was derived from the usually accepted composition of carbonic acid (Lavoisier).

In determining the relative weights of these atoms, Dalton has rigidly followed the law of greatest simplicity, which he afterwards laid down in his chapter on "Chemical Synthesis," single compounds of two elements being considered as binary (in the sense of containing two atoms only), and the lighter of two compounds having ascribed to it the simpler structure. All the numbers in this earliest table, it is interesting to note, are derived from analyses performed by chemists of reputation, and generally accepted by the chemists of the time ; not one of them appears to be due to Dalton himself. It is from the analyses of water, ammonia, sulphuric acid, and carbonic acid, that all the numbers are calculated, the law of combination in multiple proportions being, as far as can be seen, assumed as the only one according to which atomic combination could possibly occur.

-  Nitrous ⁽²⁴⁹⁾ Acid
 Nitrous Gas.
 Nitric Acid  Nitrous acid
 Water
 Ammoniac
 Gasless oxide of carbon.
 Carbonic Acid
 Alcohol? Ether?
 Sulphureous Acid
 Sulphuric Acid

-  Alcohol?  Alcohol.
 Ether?
 Carbonated hydrogen gas 
 Hydrate of carbon, or
 Carbonated aqueous vapour,
 Gas. oxide of carb. & hydrogen
 Nitrous Ammoniac = 1 Acid, 1 Am. Water


We may here refer to a fact of some importance, viz. that the mention of carburetted hydrogen, derived from stagnant water, in the paper read 1803, but published in 1805, the experiments having been performed in 1804, proves that the statements contained in the paper published in the above year were brought up to date by their author, who, as secretary of the Society at the time, would of course have ample opportunity of doing so.

. Page 249

⊙⊙⊙ Nitrous oxide.

⊙⊙ Nitrous gas.

⊙⊙⊙ Nitric acid. ⊙⊙⊙ Nitrous acid.
⊙⊙

⊙⊙ Water.

⊙⊙ Ammoniac

⊙● Gaseous oxide of carbon.

⊙●● Carbonic acid.

●⊙ Alcohol? ether?

⊕⊙ Sulphureous acid.

⊙⊕⊙ Sulphuric acid.

●⊙● Alcohol? ●⊙● Alcohol.
⊙

●⊙● Ether?

Carbonated hydrogen gas ●⊙

●⊙ Gas. oxide of carb. and hydrogen.

Nitrat ammoniac = 1 acid 1 am. 1 water.



This page (reproduced in facsimile on Plate 4)

contains the symbols corresponding with the substances mentioned on the preceding page of the Notebook. Symbols of a few compounds are added of which the composition is not given in the table. These are of nitrous acid, alcohol, and ether, the gaseous oxide of carbon and hydrogen, and nitrat ammoniac, and they have probably nearly all been subsequently inserted. The most important of these is no doubt nitrous acid, the formula for which is composed in accordance with Dalton's famous experiment on the combination of nitrous gas with the oxygen of the air.

The account of this experiment is contained in his paper entitled "Experimental Enquiry into the Proportions of the several Gases or Elastic Fluids Constituting the Atmosphere," read 12th November 1802, and published in 1805, in the same volume of the *Memoirs* with his later paper on the "Absorption of Gases." The account there given (*Memoirs*, i. p. 249) is as follows :—

"2. If 100 measures of common air be put to 36 of pure nitrous gas in a tube $\frac{3}{10}$ ths of an inch wide and 5 inches long, after a few minutes the whole will be reduced to 79 or 80 measures, and exhibit no signs of either oxygenous or nitrous gas.

"3. If 100 measures of common air be admitted to 72 of nitrous gas in a wide vessel over water, such as to form a thin stratum of air, and an immediate momentary agitation be used,

there will, as before, be found 79 or 80 measures of pure azotic gas for a residuum.

“4. If, in the last experiment, *less* than 72 measures of nitrous gas be used, there will be a residuum containing oxygenous gas ; if *more*, then some residuary nitrous gas will be found.”

The conclusion to which the experiment led him is stated in the significant words : “ These facts clearly point out the theory of the process : the elements of oxygen may combine with a certain portion of nitrous gas, or with twice that portion, but with no intermediate quantity. In the former case *nitric* acid is the result ; in the latter *nitrous* acid : but as both these may be formed at the same time, one part of the oxygen going to *one* of nitrous gas, and another to *two*, the quantity of nitrous gas absorbed should be variable.”

These results have been much discussed, but at present the interesting question is not *how* did Dalton manage to obtain these numbers, but *when* did he obtain them ? It is obvious that this statement, if made by Dalton at the date on which the paper was read, November 1802, would indicate that he had recognised the experimental fact of combination in multiple proportions long before he had adopted the atomic theory of chemical combination. The evidence of the laboratory notebooks on this point is unfortunately not quite conclusive, as the earliest record contained in them is dated November 1802, and may possibly

have been preceded by some other containing an account of the experiments in question. The evidence which can be gathered, however, goes to show that both the experimental results and the explanation, as in the case of the carburetted hydrogen, are of a later date than that upon which the paper was read. Dalton certainly became aware at an early date that the proportions in which the two gases unite depend a good deal on the circumstances of the experiment. Thus on p. 122 (Notebook, i.), 21st March 1803, we read in connection with some experiments on the solubility of nitrous gas in water: "Nitrous gas—1.7 or 2.7 may be combined with oxygen, it is presumed." On p. 129 of vol. i. of the Notebook, under the inauspicious date of 1st April 1803, is a list of experimental results obtained with nitrous gas and common air. In nearly every case a note is added as to whether the mixture of the two gases has been made rapidly or slowly, and the numbers show that more nitrous gas is absorbed when the mixture is rapidly made. Near the bottom of the page there is a note; "Query, is not nitrous air decomposed by the rapid mixture?"

This certainly seems to indicate that Dalton at that date, nearly six months after the reading of the paper, had not arrived at the conclusion so definitely expressed therein.

The actual numbers quoted in the *Memoirs* are found unaccompanied by any explanation on

p. 305, in a part of the book dated somewhere between 10th October and 13th November 1803, a month or so after the first atomic weight table had been drawn up. The passage is as follows :—

Notebook, vol. i. p. 305

Nitrous Gas.

It appears that 100 com. air
 + 36 nit. gas
 give 79 or 80 azot,
 and that 100 com. air
 to 72 nit. gas, in a broad vessel, and
 suddenly mixed, also give 79 or 80 azot,
 and if 100 com. air be put to 100 nit. gas
 as above, and just agitated, there will be 24 or 25 nit. gas left,
 supposing 2 or 3 per cent azot in the nit. gas.

That this particular experimental result was not prominently before Dalton's mind during the very earliest stages of the development of his theory is further shown by several striking facts. In the first place, we have a little piece of indirect evidence afforded by the following calculation found on p. 246 of the Notebook (September 1803) :—

"Cavendish, 10 Az. + 26 Oxy. gave acid by spark. If this was nitrous, then 10 Az. + 39 Oxy. = nitric acid.

Lavoisier says :—

$$\begin{array}{rcl}
 & \text{By weight.} & \\
 \text{A.} & \text{Oxy.} & \\
 20\frac{1}{2} + 43\frac{1}{2} & = & 64 \text{ nit. gas.} \\
 & \underline{36} & \\
 20\frac{1}{2} + 79\frac{1}{2} & = & \text{nit. acid.}
 \end{array}$$

This will perfectly agree with Mr. Cavendish."¹

¹ This last remark is scored out in the manuscript.

Lavoisier's *Elements of Chemistry* must have been one of the sackload of books to which Dalton is said to have confined his reading, for it is there that is to be found the clue to the meaning of this calculation. On p. 286 of the English translation of that work (2nd edition, 1793) we find the following passage dealing with the composition of nitric acid :—"Mr. Cavendish, who first showed by synthetic experiments that azote is the base of nitric acid, gives the proportions of azote a little larger than I have done ; but as it is not improbable that he produced the nitrous acid and not the nitric, that circumstance explains in some degree the difference in the results of our experiments." In the passage cited above Dalton is obviously testing the truth of this suggestion by calculation from Cavendish's numbers, and immediately below the passage quoted he gives Lavoisier's own numbers, which agree pretty closely with the amended result of Cavendish.

It will be seen that Dalton has converted nitrous into nitric acid by adding to the former half as much oxygen as it already contains. If we calculate the amount of oxygen from Dalton's own results, however, the number arrived at is quite a different one. Taking nitrous acid as two atoms of nitrogen and three of oxygen, whilst nitric acid is one of nitrogen and two of oxygen (his own assumption), it will be seen that the amount of oxygen to be added is not one-half but

one-third of that already present in the nitrous acid. The same conclusion is reached if the calculation be based not on the theoretical view, but on the actual numbers obtained by Dalton, as quoted on p. 35. Allowing for the specific gravity of nitrogen, oxygen, and nitrous gas, as given in the table (p. 41), 72 volumes of nitrous gas and 20 of oxygen correspond with 79.3 and 22.5 parts by weight; 101.8 parts by weight of nitrous acid therefore require 22.5 parts by weight of oxygen to convert them into nitric acid. Cavendish's acid made up of 10 of nitrogen and 26 of oxygen by volume, or 9.7 and 29.3 by weight, would then require, according to Dalton's experiment, $\frac{39 \times 22.5}{101.8} = 8.6$ parts by weight, or nearly 8 volumes of oxygen instead of the 13 which have been added in the notes. It appears from this, therefore, that in September 1803, the date of the first atomic weight table, Dalton had not adopted his well-known view as to the relation of nitrous to nitric acid. The conclusion that Cavendish's numbers could by this supposition be brought into agreement with Lavoisier's has afterwards been crossed out, perhaps after the very experiment which we are discussing had been made.

At the same time it is certain that Dalton, before the composition of his first atomic weight table in September 1803, had noticed that in some experiments a simple ratio was found between the amounts of nitrous gas with which a

given volume of oxygen combined under different circumstances. This is seen from the following extract from the Notebook, i. p. 132, dated 4th August 1803:—"It appears, too, that a very rapid mixture of equal parts com. air and nitrous gas, gives 112 or 120 residuum. Consequently that oxygen joins to nit. gas sometimes 1.7 to 1, and at other times 3.4 to 1."

It by no means follows, however, that he had at that time devised the explanation that in one case nitrous acid, and in the other nitric acid, was formed. It seems rather as though this were another instance in which "no correct notion" of the actual relations was formed "until the atomic theory was introduced and applied in the investigation." However this may be, Dalton did not include the quantitative composition of nitrous acid in any of the earlier atomic weight tables, although nitrous oxide, and nitrous gas, about the composition of which he had made no experiments, both found a place in all of them, and this of itself renders it very unlikely that the atomic theory was suggested by this particular experiment about nitrous gas and oxygen.

The formula of nitrous acid does indeed occur, as we have seen, on p. 249 of the Notebook, but its position on that page, by the side of the column of symbols, gives some colour to the view that it may have been added later.

Page 250

On the position of the other page if nitric acid and other compounds of azote be such

				A.	Ox.
then	Nitrous oxide	.	.	58.6	41.4
	Nitrous gas	.	.	41.4	58.6
and	Nitric acid	.	.	26	74
	Cavendish	.	.	27.7	72.3
	Lavoisier	.	.	20 $\frac{1}{2}$	79 $\frac{1}{2}$
	Davy	.	.	29 $\frac{1}{2}$	70 $\frac{1}{2}$

The theory above gives 1.43 for Priestley's test.

N.B.—9th September. Tried Cavendish's experiment in 1 hour constant turning the machine in good order—about 20 grs. measure of air were reduced to 16; remainder 2 $\frac{1}{3}$ oxygen.

This extract contains a calculation of the composition of the oxides of nitrogen from the numbers given for oxygen and nitrogen which had been obtained by the analysis of water and ammonia, an independent check of great value on the validity of the atomic theory of combination, and on the accuracy of the numbers adopted. The received numbers for nitric acid are quoted, and, as will be seen, the results of different chemists differ more from one another than from the calculated ones.

Although the numbers contained in the first table were not due to Dalton himself, he lost no time in endeavouring to confirm them by experiments of his own. On 9th and again on 10th September

he repeated Cavendish's experiment on the composition of nitric acid. The experiment of the 10th is described as follows (Notebook, i. p. 213):—

“10th September, Composition of nitric acid.—Mr. Cavendish's experiment. Took 17 grain measures of air $\frac{1}{3}$ azotic, and $\frac{2}{3}$ oxygenous, in a glass tube $\frac{1}{8}$ inch diameter: electrified it almost incessantly for four or five hours. It was gradually reduced to 4 grain measures, $2\frac{1}{3}$ of which were oxygen. It was confined by water having no oxygen, but $\frac{4}{5}$ impregnated with azot. The spark was taken principally, but sometimes small shocks were used.

CALCULATION

		Azot.	Oxygen.
17 grains . . .	.	$5\frac{2}{3}$	$11\frac{1}{3}$
Residue 4 grains . . .	.	$1\frac{2}{3}$	$2\frac{1}{3}$
Disappeared . . .	.	4	9
Relative wts. . .	.	24	63
1 az. to 2 oxy. } individual particles }	.	4	11.3
Are as . . .	.	24	67.8 "

[TABLE

Page 258

19th September 1803

TABLE OF THE SPECIFIC GRAVITIES, ETC.

	Sp. gr.	Wt. of ult. at.	Diameters of particles elastic. to water 1.
Hydrogen gas	.077	1	10.5
Oxygen gas	1.127	5.66	8.5
Azotic gas	.966	4	8
Compounds.			
Nitrous oxide 2 A. 1 O.	1.610	13.66	10.2
Nitrous gas 1 A. + 1 O.	1.102	9.66	10.3
Nitric acid	2.440	15.32	9.5
Sulphur		14.4	
Charcoal		4.4	
Phosphorus		7.2	
Phosphuretted hydrogen .		8.2	
Gaseous oxyd. carb. 1 C. 1 O.	1.000	10.1	11 +
Carbonic acid	1.500	15.7	11
Carbonated hydrog. 1 to 1	.660	5.4	10 +
Ammoniac gas	.580	5.00	10.2
Sulphureous acid	2.265	20.00	10.2
Sulphuric acid		25.7	
Sulphuretted hydrog. . .	1.106	15.4	12
Water vapour	.700	6.66	10.6
Ether 2 Carb. + 1 H. .	3.47	9.8	7 +
Alcohol 2 Carb. + 2 H. 1 oxy.		16.46	

The table on this page shows that Dalton lost no time in applying his results to the solution of the problem which had suggested them. The weights employed differ to some extent from those used a fortnight earlier, and are applied in conjunction

with the specific gravities of the gases to ascertain the relative diameters of the particles, by the method already described (p. 25). In this particular table the particle of standard diameter is not that of hydrogen but that of liquid water, so that the specific gravities of the gases have to be divided by $833\frac{1}{3}$, the density of liquid water compared with that of air, and the weight of the ultimate particles by 6.66, the weight of the atom of water.

The value for hydrogen should be 11.7. The results show that, with a few exceptions, the diameters of the different atoms *are* different, and Dalton was, therefore, so far justified by facts in supposing that the uniform mixture of gases might be brought about by a difference in the sizes of their particles.

Page 260

Ultimate atoms of gases in the order of their Specific Gravities:—

1.	{	Hydrogen	.	.	.	.	1
	{	Azot	.	.	.	.	4
2.		Carbonated hyd. gas.	.	.	.	.	5.4
	{	Oxygen	.	.	.	.	5.5
	{	Phosphorated hydrogen	.	.	.	.	8.2
	{	Nitrous gas	.	.	.	.	9.5
	{	Gaseous oxide of carbone	.	.	.	.	10.1
	{	Carb. aqueous vapour	.	.	.	.	11.0
3.		Nitrous Oxide	.	.	.	.	13.5
		Sulphurated hyd. gas	.	.	.	.	15.4
		Carbonic Acid gas	.	.	.	.	15.4

Here we find the atomic numbers used to test the theory suggested in Dalton's paper on the absorption of gases, viz. that the solubility of a gas depends on the weight of its ultimate particle. If this table be compared with the table of solubilities given in the paper on the absorption of gases we see that the order is nearly the same (*Memoirs*, i. p. 272).

"BULK ABSORBED, THE BULK OF WATER BEING UNITY

$\frac{1}{64}$ Azotic gas, hydrogenous gas, carbonic oxide.

$\frac{1}{27}$ { Oxygenous gas, nitrous gas, carburetted hydrogen gas,
from stagnant water.

$\frac{1}{8}$ Olefiant gas of the Dutch chemists.

1 Carbonic acid gas, sulphuretted hydrogen, nitrous oxide."

As already noticed carburetted hydrogen gas from stagnant water has been inserted some time after the reading of the paper.

The carbonated hydrogen gas of the table in the Notebook is olefiant gas, whilst carbonated aqueous vapour ($11 = 5.5 + 4.4 + 1$) is the gas which was afterwards proved to be a mixture of carbonic oxide and hydrogen.

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22nd December 1803

Proportions of compounds according to theory :—

	Azote.	Oxy.
Nitrous oxide . . .	62	38
Nitrous gas . . .	42.1	57.9
Nitric acid . . .	26.7	73.3

DAVY'S EXPTS.

			Azote.	Oxy.
Nitrous oxide	.	.	63.3	36.7
Nitrous gas	.	.	44.05	55.95
Nitric acid	.	.	29.5	70.5

Dalton here recurs to the agreement between theory and experiment with regard to the oxides of nitrogen, the atomic weights of the last table in which oxygen is taken as 5.5 being used. This entry is of particular interest, because the date which it bears, 22nd December 1803, is that of Dalton's first lecture at the Royal Institution. There seems to be no doubt that Dalton utilised the various tables just discussed in these lectures and took the notebook containing them with him to London. We may even imagine that this special comparison arose from a personal challenge from Davy, who, with regard to the atomic theory, sustained the part of the "sceptical chymist," to test Dalton's latest results. The calculations are given on the opposite page of the Notebook (261), and it is interesting, and perhaps consoling, to observe that the composition of nitrous oxide is quite wrongly calculated, the atomic weight of nitrogen having been, by a slip, taken as 4.5 instead of 4. The real numbers should be azote 59.2, oxygen 40.8, which, by the way, do not agree with the experimental figures nearly so well.

Of nearly the same date as the tables quoted

above, is a classified list of formulæ (pp. 361-353, 12th October 1803), which presents some points of interest. The alternative symbols here proposed are interesting in view of Dalton's great repugnance to the alphabetic symbols afterwards introduced by Berzelius. This list is marked by the same characteristics as the preceding ones. Olefiant gas is mentioned as carbonated hydrogen gas, but marsh gas is not referred to.

Page 361

12th October 1803

New theory of the constitution of the ult. atoms of Bodies.

Characters.					Or thus
Ⓕ Hydrogen	.	.	.	.	⊙
Ⓐ Azote	.	.	.	.	⊕
○ Oxygen.	.	.	.	.	○
● Carbon or charcoal	.	.	.	.	●
Ⓔ Sulphur	.	.	.	.	⊕
Phosphorus	.	.	.	.	⊙

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Binary Compounds.

- ⊙○ Water.
- ⊙⊕ Ammonia.
- Gaseous oxide of carbon.
- ⊕○ Nitrous gas.
- ⊙ Carbonated hydrogen gas.
- ⊕○ Sulphureous Acid.
- ⊕⊙ Sulphurated Hydrogen.
- ⊙○ Phosphorous acid.
- ⊙⊙ Phosphorated Hydrogen.

Ternary Compounds.

$\bigcirc\bigcirc\bigcirc$	Nitrous oxide.
$\bigcirc\bigcirc\bigcirc$	Nitric acid.
$\bigcirc\bullet\bigcirc$	Carbonic acid.
$\bigcirc\oplus\bigcirc$	Sulphuric acid.
$\bullet\bigcirc\bullet$	Ether.
$\bigcirc\gamma\bigcirc$	Phosphoric acid.

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Compounds of 4 Particles.

$\begin{array}{c} \bullet\bigcirc \\ \bigcirc\bigcirc \end{array}$	Alcohol ?
$\begin{array}{c} \bullet\bigcirc \\ \bigcirc\bigcirc \end{array}$	Sugar.

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Compounds of 5 Particles.

$\begin{array}{c} \bigcirc \\ \bullet\bigcirc\bullet \\ \bigcirc \end{array}$	Alcohol.
$\begin{array}{c} \bigcirc\bigcirc \\ \bigcirc\bigcirc \end{array}$	Nitrous acid.

One point still remains for discussion, the influence of Richter's work on Dalton's ideas. At what exact period Dalton became acquainted with this work it is difficult to say, but that his theory was in any way suggested by it can hardly be seriously maintained in view of the fact that the early tables contain no trace of it, whilst it would have been extremely easy for Dalton, if possessed of Richter's tables, to have worked out the weights of the ultimate particles of the chief bases. This matter is more fully treated on p. 91, in the discussion of the special numbers used by Dalton in his various atomic weight tables.

The view expressed by Debus (p. 10) that the use of the term "specific gravities" by Thomson in his account of the atomic theory implied the acceptance of the law of equal volumes by Dalton in 1804 is also seen to be incorrect. Dalton expressly states in 1803 (see extract from Notebook, p. 246), quoted on p. 27, that the specific gravities of different elastic fluids and the specific gravities of their particles are not the same thing. He never appears to have believed in the "law of equal volumes," and this only occurred to him as a possible alternative, at once shown to be inconsistent with fact, to the statement which he recognised as the true one, viz. "that no two elastic fluids agree in the size of their particles."

Dalton's attitude towards the law of combination by volume, which, enunciated by Gay-Lussac in 1808, has since become of such fundamental importance in chemical theory, is more easily understood when we perceive how firmly he had been led to believe in the unequal size and number of the particles in different gases. So long as we hold the view that the atomic theory was inspired by the experimental discovery of the law of combination in multiple proportions, it remains almost incredible that its founder should have denied his adherence to such a brilliant extension of the same principle. Gay-Lussac's law, interpreted by the atomic theory, leads at once to the conclusion that the numbers of particles in equal

volumes of the different gases are either equal or stand in some simple ratio to each other. This conclusion seemed to Dalton to be contradicted both by experimental, and, as we have seen, by theoretical considerations. The results of his own experiments, and those of many other chemists, tended to show that the proportions by volume in which gases enter into combination are neither exactly equal nor in simple multiples, but only approximately so. With regard to the special gases, Dalton's opinion fluctuated with the results of his experiments. Hydrogen and oxygen were at one time supposed to combine in the proportion of 2 : 1 (*New System*, ii. p. 275); at another as 1.97 : 1 (*New System*, ii. p. 560); again as 1.85 : 1.00 (August 1804). His view is well expressed in a letter to Berzelius, dated 20th September 1812 (see p. 159). "The French doctrine of *equal measures* of gases combining, etc., is what I do not admit, understanding it in a mathematical sense. At the same time I acknowledge there is something wonderful in the frequency of the approximation."

To this opinion he adhered until the close of his life, and in the Appendix to the last part of the *New System*, p. 349, he says: "The combinations of gases in equal volumes, and in multiple volumes, is naturally connected with this subject. The cases of this kind, or at least approximations to them, frequently occur; but no principle has

yet been suggested to account for the phenomena ; till that is done I think we ought to investigate the facts with great care, and not suffer ourselves to be led to adopt these analyses till some reason can be discovered for them."

It is interesting to note that, although Dalton's experiments were less accurate than those of Gay-Lussac, yet his conclusion was "in a mathematical sense" the more correct. Accurate determinations of density have shown that the molecular volumes of gases are not exactly equal, but that the nearer a gas is to its critical temperature the smaller is its molecular volume. In the case of gases like ammonia, chlorine, and sulphur dioxide, this difference amounts to from 1 to 2 per cent.

The evidence afforded by the foregoing extracts as to the origin of the atomic theory of chemical combination, may be briefly summed up as follows :—Dalton's own statement, made after an interval of seven years, attributes a purely physical origin to the theory, and this is confirmed by the fact that in the earliest table of atomic weights (6th September 1803) the relationships exhibited between the several oxides of nitrogen, sulphur, and carbon, are not founded upon direct experimental evidence, but upon an assumption derived from the physical theory. On the other hand, it is equally clear that a month before the compilation of the first atomic weight table, Dalton had performed an experiment which

showed him that oxygen could be made to combine with quantities of nitrous gas represented by the numbers 1 and 2. If, however, this experiment had inspired Dalton with the idea of the atomic theory, it is scarcely credible that in the table drawn up only a month afterwards, the atomic weight of nitrous acid, upon which the whole question turns, should not have been included.

The balance of evidence is, therefore, strongly in favour of the statement made in London by Dalton himself in 1810, that he was led to the atomic theory of chemistry in the first instance by purely physical considerations, in opposition to the view, hitherto held by chemists, that the discovery by Dalton of the fact of combination in multiple proportions led him to devise the atomic theory as an explanation.

It, therefore, becomes necessary for us to modify our view as to the foundation of the atomic theory. There seems to be no doubt that the idea of atomic structure arose in Dalton's mind as a purely physical conception, forced upon him by his study of the physical properties of the atmosphere and other gases. Confronted, in the course of this study, with the problem of ascertaining the relative diameters of the particles, of which, he was firmly convinced, all gases were made up, he had recourse to the results of chemical analysis. Assisted by the assumption that combination always takes place in the simplest

possible way, he thus arrived at the idea that chemical combination takes place between particles of different weights, and this it was which differentiated his theory from the historic speculations of the Greeks. The extension of this idea to substances in general necessarily led him to the law of combination in multiple proportions, and the comparison with experiment brilliantly confirmed the truth of his deduction. Once discovered, the principle of atomic union was found to be of universal application. Nothing essential has since been added to our knowledge of the laws of chemical combination by weight. To Dalton must be ascribed the rare merit of having, by the application of a single felicitous idea to a whole class of the facts of chemistry, so completely comprehended the prevailing relations, that his generalisations have sustained without alteration the labours and changes of almost an entire century.

CHAPTER II

DALTON'S SCIENTIFIC DIARY, 1802-1808

AN examination of the record of Dalton's experimental work during the period in which he was elaborating the atomic theory, and which culminated in the publication of the first part of the *New System of Chemical Philosophy* in 1808, entirely confirms the non-chemical origin of his great conception. It is at once apparent that his attention was at first directed almost entirely either to purely physical phenomena, or to those lying on the borderland of physics and chemistry. The solubility of gases in water and the diffusion of gases, together with the laws of heat, were the main subjects of investigation, chemical work being restricted to the analyses which these researches rendered necessary.

Immediately after the appearance of the first table of atomic weights in his Notebook, however, purely chemical research begins. In the year 1803 chemical analysis had attained but a low standard of accuracy, especially in its application

to gases, and the results obtained by different observers, all of repute, differed among themselves by many units per cent. Nitric acid, for example, contained, according to Cavendish, 72.3 per cent of nitrogen, according to Lavoisier 79.5, and according to Davy 70.5, whilst the statements as to the composition of sulphuric acid were even more discrepant.

In order to test the application of the theory of atoms of different sizes and weights to chemical phenomena, Dalton therefore at once set to work to repeat the analyses both of his predecessors and contemporaries, and to institute new ones of his own. Only three days after he had written in his Notebook the first atomic symbols with which we are acquainted, he repeated Cavendish's celebrated experiment on the composition of nitric acid (p. 39), and in the following autumn he began the series of researches on the gaseous compounds of carbon, which enabled him to recognise the simple relation between olefiant gas and stagnant gas.

As Dalton advanced in this direction the plan of the *New System of Chemical Philosophy* gradually developed in his mind, and we find him turning in 1806 to the composition of salts, to the chemistry of the metals, and to general systematic work.

It is especially in the investigations on heat that Dalton's characteristic mental attitude is laid open. A few experiments suggest a sweeping

generalisation, which is at once written down in the form of a query and then tested by a further series of experiments. Nearly all the fundamental laws of heat which are stated in the *New System* appear in the notebooks in this form, together with many other conjectures, which failed to stand the test of experiment.

In the following pages a general account is given of the nature of the work done during the successive months of each year, accompanied by a few quotations of passages which illustrate the author's characteristic methods of work and thought.

The earliest date to be found in the notebooks is September 1802, so that the work embodied in the papers entitled "The Power of Fluids to conduct Heat" (read 12th April 1799), "The Heat and Cold produced by the Mechanical Condensation and Rarefaction of the Air" (read 27th June 1800), and "Experimental Essays on Gases" (read during October 1801), all of which were published in the *Memoirs of the Literary and Philosophical Society of Manchester*, vol. v. part ii. (1802), and "On the Tendency of Elastic Fluids to Diffusion through each other," read 28th January 1803, and published in vol. i. of the second series of the same Memoirs (1805), is not to be found among these manuscript records.¹

¹ References [] are to the successive volumes of the notebooks.

1802

The last four months of this year were occupied with experiments on lime water, on the carbonic acid in air (*Manchester Memoirs* (2), i. 253), and on the solubility of carbonic acid, air, and other gases in water.

29th October 1802.—On this date Dalton read a paper before the Society “On the Proportion of the several Gases or Elastic Fluids constituting the Atmosphere; with an Enquiry into the Circumstances which distinguish the Chymical and Mechanical Absorption of Gases by Liquids” (published in *Manchester Memoirs* (2), i. 244; the date appended to the printed paper is 12th November 1802).

[i. 90, 91]. 26th December.—Boiling points of sulphuric and nitric acids of different strengths.

1803

January, February, and March were chiefly occupied with work on the solubility of gases in water.

[i. 81].—“2600 grs. water may be said to take

35 Azotic gas . . .	1.35	1.6
38 Hydrogenous gas . . .	1.46	1.7
60 Oxygenous gas . . .	2.31	3.0
146 } Nitrous gas . . .	{ 5.6 }	8 or $\frac{1}{12}$ nearly.”
156 }	{ 6.0 }	

The numbers of the first column represent the

solubility per hundred vols. of water ; those of the second column have been added later on, and are the results of experiments which Dalton considered to be more accurate.

[i. 96-120].—These pages are entirely filled with speculations as to the arrangement of the particles of a gas dissolved in water, especially at its surface, the nature of which may be judged from the following extract, dealing with the equilibrium of the exterior gas with that dissolved in the water :—

[i. 99, 100].—"Query, is it not two atmospheres pressing one against the other : both being constituted of geometrical progressions of very different ratios ? One slowly and the other very rapidly running off in density ?

"To investigate the preceding query it will be proper to consider what kind of geometric series will take place at the surface of the water.

"Let the particles of air to water at the surface of contact be 1 to 100, and let $F(29\frac{1}{2}$ inch M.) = force exerted by the whole on the surface, the whole force of atmosphere being 30 inches. Thence the first surface of particles will press with $F/100$ force, and all the rest must press with the same Force.

"If we take the whole force of the atmosphere on the water, then the diminution of the series = $1/100$ in force, or each particle below must be $1/100$ farther of the upper one, the original dis-

tance being unity : the distances at different points may therefore be found as under :—

I.OI = R.	Diameter of particles.	Whole distance from surf.	Sum of particles.	Remr. of sum to infinity.
I.OI ¹⁰	I.I046	11.5	10.3	89.7
I.OI ⁵⁰	I.6446	66	40	60
I.OI ¹⁰⁰	2.7048	173.2	63.4	36.6
I.OI ¹⁵⁰	4.4485	349	77.8	22.2
I.OI ²⁰⁰	7.316	639	86.5	13.5
I.OI ³⁰⁰	19.789	1898	95 -	5 +

[i. 112]. 6th March.—“It now appears more than probable that in all cases

“Hydrogen and azotic gases in water have their particles 4 times the distance that they have incumbent = $1/64$ or 1.5625 per cent, and oxygen gas 3 times = $1/27$ density = 3.7.” (Compare *Manchester Memoirs* (2), i. 272.)

A few experiments on diffusion, and a number on the combination of nitrous gas with oxygen, were also carried out during these months, a paper being read on 14th January before the Manchester Society on the “Spontaneous Intercourse of Different Elastic Fluids in Confined Circumstances,” no account of which has been published.

[i. 133]. 1st to 6th April.—Experiments on the combination of nitrous gas with oxygen, and on the solubility of gases. April 6th is noted as “End of Expts. of this sort till after midsummer 1803.” The remainder of the month of April, and the

whole of May and June were devoted to researches on the phenomena of heat, expansion of liquids, expansion of water in different vessels, force of steam, etc.

[i. 161]. *5th May*.—"It appears more than probable that the expansion of all liquids (bulk for bulk), from freezing to boiling, is reciprocally as their specific heat,—and that all liquids require (bulk for bulk) the same quantity of heat to be added to them in their lowest state to make them boil under the atmospheric pressure."

6th.—"Tried a saturated solut. of com. salt in water in the same bulb as the pure water. It gave 348 parts of expansion from 57° to boiling water; to which add 21 for the glass, we have 369. Now about 110 more should be allowed for salt and water by reason of 57° or more below and 12° above. This makes 479 for salt and water in all. The expansion of pure water for the same is 363. This gives the capacity of water to sat. salt and water nearly as 10 to 7.5. Gadolin makes it .7926; but it is probable he is too much by taking the zero too high."

July of this year was given up to the annual holiday, no entries being found for it after the 5th, whilst the next date recorded is

[i. 188]. *3rd August*.—"It appears from the recent observations on Helvellyn that the vapour point falls about 1° in 200 yards ascent nearly."

August. — Experiments on the solubility of gases, a few observations on the combination of

nitrous gas with oxygen, and some experiments on diffusion, the last of these being carried out by exposing a phial filled with the gas, and sometimes provided with a tube, to the air for a few minutes, and then examining the residual gas.

[i. 244-260]. *September*.—Here occur the tables of atomic weights, etc., as already quoted (pp. 26-44).

[i. 215-219].—These pages contain the diagrams of gases dissolved in water, published in the *Manchester Memoirs* (2), i. 285, Plates 2 and 3 (1805). In the Notebook the two diagrams of particles at a distance of 3 to 1 (density $1/27$) are ascribed to oxygenous and nitrous gas, whilst in the *Memoirs* carburetted hydrogen has been added, this gas having been, as we have already seen, first examined in 1804 (p. 29).

A few analyses of air were also done during the month.

October.—Absorption of nitrous gas by water and combination of this gas with oxygen (see p. 35). In this month Dalton commenced his work on the gaseous compounds of carbon, experimenting on the gases obtained by the incomplete combustion of ether and alcohol vapours, and by heating wood, wet charcoal, etc. No less than seventy experiments on ether vapour are recorded during the month, and new formulæ for ether and alcohol continually recur in the notes, devised to explain the results of special experiments.

An account of the state of knowledge on this subject and the reasons which induced him to commence the investigation is given by Dalton in his notes for the lectures at the Royal Institution 1810 (p. 116).

The following passage written in October summarises the results at which Dalton had arrived at that date. The "carb. hyd." of this table is shown by the contents of the preceding pages in the Notebook to be some product obtained from ether vapour:—

	Ox.	Carb. acid.	Dimin. upon original.
[i. 294].			
100 pure carb. hyd. should take	186	and make	120
			1.56
100 pure gaseous oxid. carb.	50	100	.5
	42 or 50	hyd. $\frac{1}{12}$ com. A.	1.4
100 pure hydrogen			
		hyd. $\frac{1}{10}$ com. A.	1.5
100 pure carb. aqueous vap.	60	56	1.04

21st October.—Paper on Absorption of gases, read before the Manchester Society. This paper contained the first published intimation of the atomic theory.

4th November.—Paper on the "Law of Expansion of Elastic Fluids, Liquids, and Vapours" (not published).

This paper embodied the results and speculations recorded in the Notebook during April, May, June, and July.

The only entry for *November* of this year is of some interest.

[i. 306]. 13th November.—“Query, does not hydrogen retain the same density in hydrogen gas, carb. hydrogen gas, oxy. hydrogen gas (aqueous vapour), sulph. hyd. gas, azotated hyd. gas (vol. alkali), phosphuretted hyd. gas.”

December.—The only work recorded consists of a few analyses of air, some experiments on the latent heat of fusion of ice, and a repetition of Hope's experiment, dated 16th December, together with the entry dated 22nd December, to which reference has already been made (p. 44).

Towards the close of the month Dalton went to London to deliver a course of lectures at the Royal Institution, the first of which was given on 22nd December.

1804

10th January.—Letter written from London to the editor of *Nicholson's Journal* expressing the opinion that the maximum density of water occurs at 32° (see p. 139).

February, March, April.—Experiments on the temperature of greatest density of water.

[i. 381, 382]. March.—On these pages is to be found the first application of the atomic theory to the compounds of the metals (p. 97).

May and June.—Diffusion, solubilities, combination of oxygen with hydrogen, and of oxygen with nitrous gas.

July.—On the 28th is found the usual “holiday” entry, dealing with air from Helvellyn.

August.—Experiments on the gaseous compounds of carbon, from ether and alcohol vapours, and from stagnant water.

[i. 269].—“New carb. hyd. from stagnant water. Contains no oxygen, and 7 or 8 per cent carbonic acid till cleared.”

This is followed by a number of eudiometric analyses, of which the following may be taken as an instance :—

32
78 oxy.
110
80 fired.
67 washed.

[i. 271].—“New carbonated from stag. water.

“It appears by a most decisive set of experiments, direct and indirect, that this gas is absorbed $\frac{1}{27}$, and therefore differs from the olefiant gas and oxy. carb. gas.”

[i. 272*a*].—“Query, is not ether after all 1 carbon and 1 hydrogen ?

●○ ether ?	○○○ olefiant gas.	●○ oxy. carbonate.
Or is ●○ ether.	●○ olef.	○○○ carb. hyd.
	●○ oxy. carb.”	

[i. 278].—“*N.B.*—The carb. hyd. in water formed thus

2 oxy. + 1 carb. = carb. acid.

2 hyd. + 1 carb. = gas in quest.

from the decomp. of 2 particles of water.



This is one of very few symbolic equations to be found in the notes.

[i. 282]. 24th August.—“ It now appears highly probable that the gas called *oxy. carbonate* in these notes is in reality a compound of *gas oxid. of carbone* and *hydrogen* in equal parts.”

[i. 283]. 24th August.—This page contains a statement showing that by this time the relation between olefiant gas and stagnant gas had become clear.

Olefiant gas.			
Meas.	Acid.	Oxy.	Dimin.
100	200	300	200
Stagnant.			
100	100	200	200

All gases containing olefiant are distinguished by the smell : the oxycarbonate and stagnant not.

[i. 287, 288].—These pages contain a list of the equivalents of the alkalis and earths, to be discussed later (p. 92).

The following “ Remarks on sulphurated hydrogen, etc., ” are interesting :—

[i. 324-326].—1. "Sulph. hyd. gas cannot be sulphur and water because in firing with oxy. sulphur is thrown down and oxy. spent.

2. The gas may then be 1 hyd. + 1 sulphur, or 2 hyd. + 1 sulphur. It seems formed from hydrogen and sulphur by passing hyd. through melted sulphur.

3. It seems probable that the *oil* which Berthollet calls *sulphur hydrogenated* is 1 sulphur and 1 hydrogen, analogous to the olefiant gas of carbone and hyd.

$\odot \oplus \odot$ Sulphuretted hydrogen.

$\odot \oplus \odot$
 $\circlearrowleft$ Hydrosulphure of lime.

$\oplus$
 $\circlearrowleft$ Sulphure of lime.

$\oplus$
 $\odot$ hydrogenated sulphur.

$\oplus \circlearrowleft$
 $\odot$ hydrogenated sulphure."

September.—Experiments with Volta's eudiometer and on ether vapour, etc. Expansion of water.

[i. 318].—Theory of oxides of metals (p. 97).

[i. 329]. 13th *September*.—"It seems very probable that azotic and oxygen gases condensed moderately would fire by the electric spark and become nitric acid."

[ii. 107] 14th *September*.—More correct tables of the sp. gr. etc. of certain gases.

	Sp. Gr. atmos. air 1	Wt. of ult. par. Hyd. being 1	Diam. of part. elas- tic to hyd. 1.
Hydrogen gas	.1	1	1
Oxygen gas	1.127	5.5	.787
Azotic gas	.966	4.2	.758
Compounds.			
Nitrous oxide (2 A + 1 ox.)	1.610	13.9	.952
Nitrous gas (1 A + 1 ox.)	1.102	9.7	.958
Nitric acid (1 A + 2 ox.)	2.440	15.2	.854
Carbonic oxide (1 C + 1 ox.)	0.84	9.8	.993
Carbonic acid (1 C + 2 ox.)	1.500	15.3	1.00
Olefiant gas (1 C + 1 H)	.905	5.3	.809
Carb. hyd. from water (1 C + 2 H)	.620	6.3	1.00
Sulphuretted hyd. (1 S + 2 H?)	1.106?	16.4?	
Vapours.			
Aqueous vap. (1 H + 1 ox.)	.700	6.5	.976
Ether (2 carb. + 1 hy.)	3.47	9.6	.652
Alcohol (2 carb. + 1 wat.)	2.00	15.1	.911
Ammon. gas (1 A + 1 H)	.580	5.2	.965

It will be seen that the numbers in the last column generally differ very considerably from each other, and must have been considered by Dalton as in very satisfactory agreement with his theory of the structure of gases.

October, November and December.—These months were occupied with experiments on heat, the rate of cooling of bodies and the expansion and temperature of maximum density of water. Papers were read by Dalton before the Manchester Society on 5th October, "On Heat," and on 30th November "Review of Dr. Hope's paper on the Contraction of Water by Heat."

1805

January.—Determination of the temperature of maximum density of water by expansion in thermometers of different materials, and by Hope's experiment under various conditions.

No entries are to be found for *February, March, April, and May*. We learn from Henry (*Life of Dalton*, p. 63) that in February Dalton went to London to purchase apparatus, and in the summer of the year delivered a course of lectures in Manchester to an audience of about 120 at two guineas each.

The last section of vol. ii. of the Notes is made up of about half a dozen of spare copies of the prospectus of these lectures, the printed side being often covered with notes as well as the blank pages.

The prospectus runs as follows :—

“ *Prospectus*
of an intended course of
Lectures on Natural Philosophy
in Manchester
by John Dalton

“ In a populous town like this, where the Arts and Manufactures are so intimately connected with various branches of Science, it may be presumed that public encouragement will not be wanting to a person qualified to exhibit and illustrate the truths

of experimental philosophy upon a liberal and extensive scale.

“Notwithstanding this it would be imprudent for one of limited resources to purchase a large and expensive apparatus adequate to the object, upon a mere presumption. Something like a certainty of remuneration in a degree may fairly be expected.

“With this view I propose, if a competent number of subscribers at two guineas each be procured, to extend the apparatus already in my possession, so as to give a course of twenty lectures on the various branches of experimental philosophy in the ensuing spring. Having for many years been engaged in the cultivation of the sciences of Mathematics and Natural Philosophy, and having lately delivered a course of Lectures similar to the one proposed in the Royal Institution at London, I may perhaps have some claim upon public confidence.

“Each subscription ticket will admit a Gentleman and a Lady or two Ladies. The Lectures will be delivered twice if the number of subscribers exceed sixty, in order to their greater accommodation.

“Those who wish to favour the undertaking will oblige me by putting down their names as early as may be on papers left for the purpose at Messrs. Clarkes’ or Messrs. Thomson and Son’s, book-sellers.”

FALKNER STREET, *Jan. 2, 1805.*

June.—Composition of nitrous oxide. Solubility of olefiant gas, nitrous oxide and nitrous gas.

[ii. 36]. *5th July*.—"It appears that stag. Gas requires $\frac{1}{2}$ of its share of oxygen, namely cent per cent before it will fire. It then becomes same bulk of gas without any acid, that is gas. oxid. of carb. and hyd.

"It again appears that olefiant gas requires its bulk of oxygen to fire—I measure then becomes nearly 4, and requires $\frac{1}{2}$ its bulk of oxygen and produces half its bulk of acid. No oxygen or acid after the first firing."

Composition of nitrous oxide, gas from boxwood, from chalk and iron, ether gas, olefiant gas, etc.

[ii. 41].—Composition of sulphuretted hydrogen by explosion with oxygen.

"It seems clear that sulph. hyd. takes twice its bulk of oxygen, and is therefore 4 times the density of com. hydrogen."



(This refers to the density of the hydrogen in the compound, see p. 61.)

July.—Sp. gr. of air, ether vapour, carbonic acid, and stagnant gas.

August.—Solubility of gases, composition of nitrous oxide, ether gas, etc.

September.—Alcohol vapour.

Nitrous gas and oxygen.

Two or three pages are occupied with an account of the colour of the precipitates produced by mercuric nitrate and lead acetate with lime-water, sulphuretted hydrogen, and alkalis, showing that Dalton was now beginning to take an interest in general chemistry.

October.—The only entry during this month is as follows :—

[ii. 123]. *6th October 1805.*—"It appears from sundry expts. that hyd. fired with oxigen gives 100 ox. for 190 hyd.:—it seems too that when the combustion is very rapid there is some trace of oxig. left in hydrogen. In slow combustion it should seem as if 100 ox. required 200 hyd. At least 60 seems right for atmos. air.

"Again repeated and 60 seems the nearest number—

$$\frac{21}{39}$$

13

185. This may be said to be 190."

60 here is the diminution produced by firing air containing 21 per cent of oxygen with hydrogen.

November. — Cooling of a thermometer in different gases.

Heat of combustion of tallow.

Dalton seems to have commenced his work on the New System at about this time (Henry's *Life*, p. 64), and this no doubt accounts for the small amount of experimental work recorded during these months.

December.—Experiments on rate of cooling, etc.
Experiments on diabetic urine.

[ii. 137]. 1st *December.*—"It seems probable that the Radiation of heat is either a constant quantity, or rather perhaps *increases* as the density decreases:—that the Abduction depends upon the proper capacity of the medium. The abduction cannot therefore decrease *exactly as the density*, because the capacity is greater in rarefied air, proved by the cold produced. It cannot be as the *cube root* of density or diameter of particles, because experience is against it. It may be as the *square root* of the density, as that nearly agrees with experiments. The square of cube root of density does not seem to agree—nor ought it."

Note (added at a later date).

"Probably the sq. of cubic root of density multiplied by capacity."

In the *New System*, i. p. 120, Dalton states his final conclusion that it varies "nearly or accurately as the cubic root of the density."

1806

January.—Temperature of maximum density of water.

February.—No entries.

March.—Experiments on the effect of breathing and combustion on air (Paper "On Respiration and Animal Heat" read 7th March 1806. Pub-

lished, *Manchester Memoirs*, ii. (Second Series), p. 15 (1813)).

The remainder of this month, together with the whole of April and May and the greater part of June, was entirely occupied (the notes extend to about fifty pages) with experiments and speculations on heat, the final results of which are embodied in the *New System*, part i.

The following extract from a short article "On heat," extending to five pages of manuscript [ii. 287-292], 23rd May 1806, is of interest as giving a very clear account of Dalton's ideas about the atmospheres of heat with which his atoms were provided.

" . . . According to this view of the subject, every atom has an atmosphere of heat around it, in the same manner as the earth or any other planet has its atmosphere of air surrounding it, which cannot certainly be said to be held by chemical affinity, but by a species of attraction of a very different kind. Every species of atoms or ultimate particles of bodies will be found to have their peculiar powers of attraction for heat, by which a greater or less quantity of that fluid will be conglomerated around them in like circumstances : this gives rise to what has been called the *different capacities* of bodies for heat or their *specific* heat. Any two bodies, the atoms of which have different capacities for heat, being placed in any medium will acquire the same *temperature*. This state consists in the several

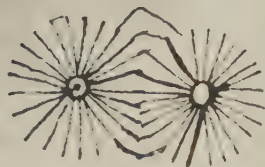
individual atmospheres of heat acquiring the same density at their *exterior surface*, or where they become contiguous. The virtual diameters of atoms of matter will therefore vary in like circumstances according to their attraction for heat; those with a strong attraction will collect a large and denser atmosphere around them, whilst those possessing a weaker attraction will have a less atmosphere, and consequently the virtual diameter, or that of the atom and its atmosphere together, will be less, though the atmospheres of both have precisely the same disposition to receive or to part with heat upon any change of temperature.

“*Temperature* may perhaps be best conceived of from a vacuum surrounded by any solid body : heat will flow into the vacuum till an atmosphere of uniform density is established within it. If more heat be added to the solid body a part of it will be given off to the vacuum ; the *density* of heat within the vacuum is to be understood as the proper measure of temperature, provided it could be obtained.

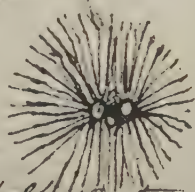
“Every atom of matter possesses the same attraction for heat, whether it is situated in a dense or rare atmosphere of that fluid ; the quantity collected therefore must depend primarily on the temperature of the medium.”

[ii. 208].—“Query, does not the quantity of heat in a given *volume* of gas vary as the *diameter* of the atoms under like pressure ? No.”

June 17th 1851
Thoughts on atom, theory
of caloric.



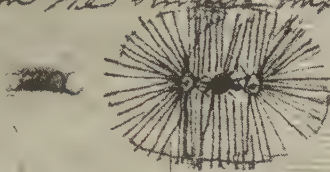
1. It is probable that in the combination or
chemical combination of two atoms
pairs, the distance between them is
partly given and it is thrown in
to the new general atom then, but
that the quantity thrown out is always
greater than the quantity so collected.



2. It is probable that the distances
of the particles or combined, using by
heat the same in the simple as the
compound, in like circumstances.

3. The theory of compound particles
cannot be spherical if one, has a
single
specific attraction for caloric, gas
and this. - The difference however
will be small.

(219)
 to *Monna Ponce* ~~double~~ units form
 a, a tube, or two protects one double
 & the other single. The colony is
 silver net & that the compound is
 of greater specific gravity than would
 arise from the simple mixture.



Every is observed *Gas* & others —

Calculation. $10 \text{ sh} + 1 \text{ hsd} = 11$ wt
 $26 \text{ oz} \quad 6.5 \text{ oz} \quad 32.5 \text{ wt}$

since 1 to 3 in weight

on the the powder — 6 wt
 19.5 wt

1 to $3\frac{1}{4}$

Other
 1st pos. — — — 15
 $162.84 \quad 45.5$

2nd pos. 1 to 2.95

Mr. The entire power of powder gas is given
 better with the old substitution

[ii. 209]. 1st June.—“I. It seems clear that the attraction of any atoms for heat must be as their diameters in an elastic state, whatever be the law of attraction.

“II. It seems also true that the law of attraction, whatever it may be, will not affect the relative quantities of heat around different kinds, in like circumstances.

“III. Further, the absolute quantities of heat around different atoms must be as the cubes of the diameters of these atoms. *Consequently all elastic fluids of given pressure and temperature contain the same heat in the same bulk.*”

This conclusion is stated in the *New System*, i. p. 70, to be untenable.

[ii. 218, 219]. 17th June.—These pages are reproduced in facsimile in Plates 5 and 6.

“Thoughts on atmospheres of caloric.”

“1. It is probable that on the coalition or chemical combination of two atoms of air, the caloric between them is partly given out and is (partly) thrown on to the new general atmosphere, but that the quantity thrown out is always greater than the quantity so collected.

“2. It is probable that the distances of the particles so combined varies by heat the same in the simple as the compound, in like circumstances.

“3. The figures of compound particles cannot be globular if one simple has a greater attraction

for caloric than another. The difference, however, will be small.

“4. Whenever three units form a particle, or two particles, one double and the other single, caloric is given out so that the compound is of greater specific gravity than would arise from the simple mixture.”

[ii. 220-2]. 21st June.—Experiments on the explosion of gaseous mixtures, of oxygen and carbonic oxide, leading to the conclusion “that both oxygen and the gas in plenty may be left after firing.”

July.—Analysis of air and oxygen.

[ii. 224]. July 26th.—“It seems to strike with peculiar force that with respect to *heat* there ought to be found two Analogies—one for the absolute quantity of heat—the other for temperature; the measures of the former will be somewhat resembling a *cylinder* in capacity—the other probably resembling a *cone*.”

August, September, and October.—During these months Dalton was busy with the composition of salts and the revision of his atomic weights (see pp. 83, 93).

[ii. 241]. 9th September.—“N.B. Sulphuretted hydrogen and sulphuric acid ought to be formed from water as carburetted hyd. and carbonic acid (p. 63) by decomposing as under :—



Therefore the sulphuretted hyd. ought to be 1 sulphur and 2 hydrogen."

[ii. 245]. "Sulphuretted Hydrogen.—From a carefully repeated trial it seems confirmed that 20 of this gas takes 30 oxygen as near as may be. The hydrogen therefore is three times the density of com. hydrogen.

"If therefore sulphur = 12

Sulphuretted hyd. = 15 = $\begin{array}{c} \odot \\ \odot \oplus \odot \end{array}$

If sulphur = 8

Then sulphuretted hyd. = 10 = $\odot \oplus \odot$."

(Compare p. 64.)

[ii. 269]. 27th September.—"Found that *fire damp* of coal mines is *carb. hyd.* pure."

November and December 1806.—The only entry is as follows :—

[ii. 258]. 2nd November.—It appears almost demonstrable that ammonia is 2 particles of azot and 2 of hydrogen united ; also that a particle of nitric acid weighs 38, and is made of what I have formerly conceived to be two particles, whence they will be marked thus—



Ammonia



Nitric Acid.



Nitrous vapour.



Oxynitric acid formed by mixing nitrous gas with an excess of oxygen.

1807

In March and April of this year Dalton delivered and repeated a course of lectures at Edinburgh.

During the earlier part of the year he was almost entirely engaged with experiments on heat and on the specific gravity and boiling points of acids. One or two new tables of atomic weights are also found, probably drawn up for the Edinburgh lectures.

[ii. 306]. 29th January.—“Heat. The densities of the exterior surfaces of elastic atoms depend entirely on the *pressure* and no ways on the *temperature*: this last influences the *bulk* of the atom only.”

[ii. 318-322]. February.—Determination of the heat of combustion of hydrogen, etc. The results are practically identical with those given in the *New System*, i. 77, but the volume of gas used and the capacity of the vessel heated are only one half of those mentioned in the latter.

[ii. 330]. February.—“Does not the *capacity* increase as the *volume* reckoning from absolute *solidity* or from the volume at absolute cold?”

[ii. 331]. Theory of the formation of ice as given in the *New System*, i. p. 137. At foot of page, “This is a most satisfactory explanation.”

On 6th February Dalton read before the Manchester Literary and Philosophical Society a

paper on "The Constitution and Properties of Sulphuric Acid," which was not printed in the journal of the Society. The alternate blank pages of this paper were utilised later on (in 1811) by the author for notes, and the paper is therefore found bound up in vol. iv. of the Notebook [pp. 192-156].

The paper consists of a critical discussion of the various authoritative analyses of the acid and of barium sulphate, accompanied by the author's own views, which are practically the same as those expressed in the *New System*, ii. 398.

The remainder of the paper treats of the density of the acid and some of its mixtures with water and the heat evolved on dilution, the latter being used to calculate the absolute amount of heat in the acid.

The following extracts are of some interest :—

"Upon the whole I think we may safely conclude from the experience already had on this subject that the quantity of sulphur in real sulphuric acid is not less than 40 nor more than 45 per cent; and consequently the oxygen not less than 55 nor more than 60 per cent."

"In corroboration of the above conclusion I might add the results of my own investigation on this subject. My enquiries not only respect the *weight*, but the *number of particles* of sulphur and oxygen which constitute an atom or smallest particle of sulphuric acid. Having found from

a comparison of the several sulphates and other neutral salts, that a particle of sulphuric acid weighs 34 times as much as 1 of hydrogen; and that one of oxygen weighs nearly 7 times as much as 1 of hydrogen: it seemed almost certain that to constitute an atom of sulphuric acid, either 2 or 3 atoms of oxygen must join to 1 of sulphur; if 2 atoms of oxygen, then one of sulphur must weigh 20; if 3 atoms of oxygen then one of sulphur must weigh 13 or 14; the latter supposition seemed most coincident with the facts in general. According to my view of the subject, therefore, sulphuric acid must be composed of 39 or 40 sulphur and 60 or 61 oxygen. It is remarkable that sulphuretted hydrogen gas seems likewise to be constituted of 1 atom of sulphur and 3 of hydrogen."

[ii. 334]. *5th March*.—"Boiled some nitric acid with a view to condense it; it began about 240°, and having boiled a few minutes the greater part was vaporised or decomposed in a moment, throwing the rest about the room, breaking the phials, burning nearly all my cloaths, hands, etc., thighs and legs marked through breeches and stockings, etc. This acid was dark coloured, but gave no elastic vapour of consequence before ebullition."

[ii. 342].—Specific gravity of sulphuric acid.—"Query, is not the *geometric mean* of any two specific gravities correspondent to the arithmetic mean of

the two ingredients? If so it will be a most important fact. Try 10 A + 5 W and see if it come 1.58. Also is not alcohol and water the same? Also is not the quantity of heat given out, proportionate to the difference between the arithmetic and geom. means of the densities?"

[ii. 343].—"It seems clear that the *geometric mean* of the two sp. gr. must be right, for it is *always* less than the arith. mean as it ought to be; and it agrees with direct expt. This regards sulphuric acid. But if it apply to alcohol we must be wrong in supposing alcohol of .82 to be *pure*; it probably contains considerable water."

[ii. 347]. *Edinburgh, 28th March*.—"It is probable the purest alcohol of .791 sp. gravity is still more than half water."

19th April.—"Is not sulphureous acid sulphuric and sulphur? Thus $\bigoplus\bigoplus\bigcirc$, its weight 48."

[ii. 348]. "Oxalic acid is probably $\bigcirc\bigcirc\bullet\bullet = 31$.

"Tartaric acid seems to be 50 by Richter.

"Citric acid is about 50 by Richter and Vauquelin."

This is the first reference to Richter which has been found. Richter's numbers for these acids were—Tartaric 1694, citric 1583 (sulphuric = 1000).

On his return from Edinburgh, Dalton was

engaged during May, June, and July in the study of the oxides and salts of the metals.

The notes include his own analytical results and observations, together with numerous compilations and comparisons of the results of others.

[ii. 421]. *July*. METALS.

	Sp. gr.	Ult. atom.	Sp. heat.
Antimony . . .	6.71	37? 50? 40	
Zinc . . .	6.86	56	.7
Manganese . . .	6.85	63	
Tin . . .	7.30	50-60	.5
Iron . . .	7.78	50	.8
Arsenic . . .	8.31	42?	
Copper . . .	8.89	56	.8
Bismuth . . .	9.82	62	.4
Silver . . .	10.5	100	1.00
Lead . . .	11.3	95	.5
Mercury . . .	13.6	166	.8

After July, Dalton was probably much occupied with preparing and passing through the press the first part of the *New System*, as the entries for the remaining part of the year and the whole of 1808 are very scanty, and for the most part consist of tables, etc., which are reproduced in that work.

The following passage is perhaps as characteristic of its author as any hitherto quoted :—

[ii. 495]. *July* 1808.—“A quire of paper such as part i. of *New System of Chemistry* weighs 14 oz. at a medium.”

CHAPTER III

DALTON'S ATOMIC WEIGHT NUMBERS

IN seeking to determine the weight of the ultimate particle or atom of a substance, Dalton at once perceived that a simple knowledge of the proportion in which the substance combined with a fixed weight of some standard substance was not sufficient, but that it was also necessary to ascertain the number of atoms of each between which the combination ensued. He was unable to perceive any more definite way of deciding this all important question than the assumption of the "Law of greatest simplicity," according to which the simplest possible formula is most probably the correct one. Admitting the uncertainty of this method of reasoning, but finding himself unable to replace it by any more trustworthy, Dalton in his first table of atomic weights, as well as in his last, remained true to the principles laid down in the celebrated chapter on "Chemical Synthesis."¹

¹ *New System*, part i. p. 214.

The actual numbers chosen by Dalton to represent the atomic weights of the elements and their compounds, varied considerably in the various tables which he published from time to time, and they are in many cases marked by wide divergence from the numbers which are now accepted, so that it becomes a matter of interest to ascertain the reasons which led him to the choice of each special number, and to see how far he depended for his data upon the analyses of others, and how far upon his own work. The attempt has been already made,¹ but the additional information now supplied by the laboratory records renders a much more complete treatment of the matter possible, and shows that some of the conclusions previously arrived at are not quite accurate.

It will be convenient in dealing with the atomic weights to divide the substances concerned into the three classes of non-metals, earths and alkalis, and metals.

Dalton's attention was at first directed almost entirely to the non-metals, their gaseous compounds, and the acids derived from them, and the laboratory notebooks contain several provisional lists of atomic weights in addition to those which have hitherto been made known.

The following table contains in chronological order all the lists drawn up by Dalton before the

¹ Roscoe, *Manchester Memoirs* (1875), [3] 5, 269.

publication of the first part of the *New System* in 1808, together with those published in the first two parts of that work, and the list supplied by Dalton to Thomson, and printed by the latter in his *System of Chemistry* in 1807 :—

TABLE A

	(1) 1803	(2) 1803	(3) 1803	(4) 1805	(5) 1807	(6) 1806	(7) 1806	(8) 1808	(9) 1810	(10)	(11)
Hydrogen .	1	1	1	1	1	1	1	1	1	1.14	1.008
Oxygen .	5.66	5.66	5.5	5.5	6	7	7	7	7	16	16
Azote . .	4	4	4	4.2	5	5	5	5	5	{ 11.4 15 }	14
Carbon .	4.5	4.4		4.3		5	5	5	5.4	12.3	12
Sulphur .	17	14.4		14.4		22	12	13	13	29.7	32
Phosphorus		7.2		7.2		9+	9.3	9	9	{ 25.7 27 }	31

(1) Notebook, i. 248, 6th September 1803.

(2) Notebook, i. 258, 19th September 1803.

(3) Notebook, i. 260, September 1803.

(4) *Manchester Memoirs* (2), i. 287 (1805).

(5) Thomson's List (1807), probably given to Thomson by Dalton in 1804, or perhaps later.

(6) Notebook, ii. 282, 23rd August 1806, and ii. 284, 14th August 1806.

(7) Notebook, ii. 247, 16th September 1806; and ii. 256, 22nd October 1806.

(8) *New System*, part i. p. 219.

(9) *New System*, part ii. p. 352.

(10) The numbers of (9) calculated to O = 16, and assuming the modern formulæ. Two numbers are given for nitrogen and phosphorus, one calculated from Dalton's formula of the hydride, the other from that of the oxide.

(11) The modern numbers, O = 16.

I. OXYGEN

Dalton uniformly adopted the atomic weight of hydrogen as unity and determined the relative weight of oxygen from the composition of water, assuming that the atom of the latter was made up of one atom of oxygen and one of hydrogen.

Columns (1) and (2), Table A.—The number 5.66 is calculated from Lavoisier's analysis of water, according to which it contains—

85 Oxygen.
15 Hydrogen.
100

Columns (3) and (4).—The reason for the change from 5.66 to 5.5 is to be found in the Notebook, i. 257.

“Note relative to the wt. of oxygen :—

“If we take $84\frac{1}{2}$ to $15\frac{1}{2}$ it gives 5.5 oxy. to 1 hyd.; but 1 measure oxy. seems to combine with 2 hydrogen: if sp. gr. of hydrogen be $\frac{1}{16}$ of oxygen it gives 5 to 1

”	$\frac{1}{11}$	”	”	5.5	”	1
”	$\frac{1}{12}$	”	”	6	”	1
”	$\frac{1}{13}$	”	”	6.5	”	1
”	$\frac{1}{14}$	”	”	7	”	1”

Column (5).—The number 6 is probably given by Thomson from recollection as the nearest whole number.

Columns (6), (7), (8), and (9).—After the appearance of Gay-Lussac and Humboldt's memoir in 1805, Dalton (*New System*, i. 274) adopted their

analysis for water, according to which it contains 87.4 oxygen to 12.6 hydrogen, or nearly 7 to 1 (6.93 to 1).

II. NITROGEN

Columns (1), (2), (3), Table A.—The number 4 for nitrogen is derived from an old analysis of ammonia (Notebook, i. 247, September 1803) by Austin (*Phil. Trans.* 1788), according to which this gas is composed of 121 parts of nitrogen to 32 of hydrogen, or about 80 per cent nitrogen to 20 per cent hydrogen.

Column (4).—Berthollet (*Journ. de Phys.* xxix. 177) obtained the more correct numbers, 121 of nitrogen to 29 of hydrogen, or 4.2 to 1.

Columns (5) to (9).—The reasons for adopting 5 as the atomic weight of nitrogen are explained in the *New System*, i. 319. From Davy's analysis of the oxides of nitrogen it appeared to be 5.6 ($O=7$), whilst from the analysis of ammonia it seemed to be 4.7. The reason for this great divergence does not lie in the experimental work, but in the fact that Dalton formulated the oxides of nitrogen as we do, but looked upon ammonia as NH . The correct numbers would, therefore, have been from the oxides, $N=6.1$ ($O=7$) and from ammonia, $N=4.7$ ($H=1$). Dalton himself considered that 5.1 more nearly represented the atomic weight of nitrogen as derived from the analysis of the oxides.

III. CARBON

Dalton seems to have adhered throughout to Lavoisier's analysis of carbonic acid gas, according to which it contains 72 of oxygen and 28 of carbon per cent. If this be so, and the atomic weight of oxygen be 5.66, then, the formula of carbonic acid being assumed as CO_2 , the atomic weight of carbon must be $\frac{28 \times 5.66}{36} = 4.4$. The number 4.5 given in the first list is probably a miscalculation. When the atomic weight of oxygen was changed to 5.5, that of carbon became $\frac{4.4 \times 5.5}{5.60} = 4.3$, and finally with $\text{O} = 7$, carbon became 5.4. In lists 6-8, however, it is made equal to 5, this being most probably simply an approximation, which Dalton, in view of the great uncertainty attaching to the numbers for the other elements, considered to be sufficiently accurate. In any case there does not seem to have been any more authoritative analysis of carbonic acid which would account for the change, and in the *New System*, i. 237, we find the statement:—

“From the various combinations of charcoal with other elements, hereafter to be mentioned, the weight of its ultimate atom is deduced to be 5, or perhaps 5.4, that of hydrogen being denoted by unity.”

IV. SULPHUR

The great variation in the numbers chosen for sulphur at various times is to be attributed to the uncertainty which existed as to the composition of sulphuric acid. The results of different observers differed so much that the choice of numbers was very difficult, and we find accordingly that several of the numbers selected are compromises between differing analyses.

The earliest number, 17 (column (1), Table A), is derived from Chenevix's analysis of sulphuric acid, *Nicholson's Journal*, v. 126 (1803), on the assumption that the acid consists of 1 atom of sulphur combined with 2 of oxygen. Thus we find the following passage (Notebook, i. 247) :—

Sulph.	Oxy.
“Chenevix $61\frac{1}{2}$ + $38\frac{1}{2}$ = sulphuric A.	
then $61\frac{1}{2}$ + $19\frac{1}{4}$ should be sulphureous.”	

“This gives the ult. part. of sulphur to oxy. 3.2 : 1, nearly.”

The number next employed (columns (2) and (4)), 14.4, corresponds with Thénard's analysis of sulphuric acid, according to which it contains—

56 Sulphur.
44 Oxygen.
100

The number 22 given in column (6) (August 1806) corresponds with the composition 61.1 sulphur and 38.9 oxygen, and, therefore, indicates

an approximation to Chenevix's number. The further development of Dalton's views on this matter may be traced by the following passages:—

[ii. 243]. “*N.B.*—The mean of all expts. on sulphuric acid is 59 sulph., 41 oxygen. Chenevix is $61\frac{1}{2}$, $38\frac{1}{2}$. Probably we may be safe in saying 60 to 40, which gives sulphur 21.”

This number does not actually find a place in any of the lists.

[ii. 246]. 16th September 1806.—“It seems that Kirwan and Klaproth will agree in sulphuric acid if we take sulphur 12, oxy. 7 and make real sulphuric acid = $\bigcirc\oplus\bigcirc$ and sulphuric acid of 1.85 = $\bigcirc\oplus\bigcirc$.

“Mr. Chenevix will agree in the composition of sulphuric acid if we adopt Kirwan on sulphate of lime, instead of him—also in giving sulphate of barytes 33 per cent acid.”

Kirwan and Klaproth differed as to the amount of water with which the real acid combined to form the most concentrated liquid sulphuric acid, the former stating it as 21 water to 79 acid, and the latter as 25 water to 75 acid. Adopting Dalton's view, 34 of concentrated acid contains 8 of water, or 23.5 per cent. We accordingly find in column (7), Table A (September 1806), that sulphur is taken as 12, real sulphuric acid being $12 + 2 \times 7 = 26$, and liquid sulphuric acid $12 + 2 \times 7 + 8 = 34$.

In comparing the composition of the various salts of the alkali and alkaline earth metals, however (Notebook, ii. 248 *et seq.*, see p. 94), Dalton

found that the same amounts of the various bases (1 atom) were saturated by 38 parts of nitric acid (2 atoms), 23 parts of muriatic acid (1 atom), 19 parts of carbonic acid (1 atom), and 34 parts of sulphuric acid. He, therefore, seems to have somewhat inconsistently assumed that the 8 parts of water contained in 34 parts of liquid sulphuric acid entered into the composition of the salts of the acid. This inconsistency was finally removed in the lists published in the *New System*, columns (8) and (9), in which Dalton, making the atomic weight of sulphur 13, takes real sulphuric acid as made up of 3 atoms of oxygen and 1 of sulphur, the compound atom therefore weighing $34 = 3 \times 7 + 13$. This corresponds with the composition 38.3 sulphur and 61.7 oxygen, whilst liquid sulphuric acid becomes $34 + 8 = 42$, containing 17.7 per cent of water (see also p. 77). The actual numbers for sulphur trioxide are 40 of sulphur to 60 of oxygen, whilst liquid sulphuric acid contains 18.4 per cent of water, an agreement which Dalton would have thought "very satisfactory."

V. PHOSPHORUS

The numbers given for phosphorus correspond almost exactly with the composition of phosphoric acid as determined by Lavoisier. He found that it contained 39.4 of phosphorus to 60.6 of oxygen, which gives 7.36 for phosphorus when $O = 5.66$,

and 7.15 when $O = 5.5$; phosphoric acid being supposed, on the model of sulphuric acid, to be made up of 2 atoms of oxygen combined with 1 of phosphorus. At the same time it is possible that the number 7.2 (columns (2) and (4), Table A) was derived from some early determination of the density of phosphuretted hydrogen, since the composition of phosphoric acid does not enter into the early tables. The number 9.3 (columns (6) and (7)) corresponds, when the atomic weight of $O = 7$, with the approximate composition, 40 per cent of phosphorus to 60 of oxygen, which is quoted in the *New System*, ii. p. 413. The final number 9 (columns (8) and (9)) results from the "facts" that phosphuretted hydrogen contains its own volume of hydrogen, and is ten times as heavy as hydrogen, the atom of the gas being regarded as made up of one atom of each of its constituents.

VI. THE ALKALIS AND ALKALINE EARTHS

The atomic weights of these bodies do not appear in the tables until August 1806, some three years after the first table had been drawn up. The following table contains the various numbers, which, as will be seen, do not vary much :—

[TABLE

TABLE B

	(1)	(2)	(3)	(4)
Potash . . .	18 ?	22 +	42	42
Soda . . .	28	26, 28	28	28
Lime . . .	22	22-10 ?	23	24
Magnesia . . .	20 ?	20 ±	20	17
Strontian . . .	42 } 38 }	44 ?	46	46
Barytes . . .	76 ?	48	68	68
Alumine . . .	(11) 36 ?	30, 40, 60 ?	—	15

(1) Notebook, ii. 284, 14th August 1806.

(2) Notebook, ii. 282, 23rd August 1806.

(3) Notebook, ii. 247, 16th September 1806, and ii. 256, 22nd October 1806, and *New System*, part i. p. 219.

(4) *New System*, part ii. p. 547.

Although Dalton did not endeavour until 1806 systematically to apply the atomic theory to explain the composition of salts, he nevertheless made occasional attempts in this direction at earlier dates, and these are of some interest as showing that his ideas were at all events uninfluenced by Richter's results, of which in 1803-1804 he seems to have been ignorant.

The very first reference to the atomic weight of the alkalis occurs in the Notebook, i. 287-288, at the end of one of the sectional notebooks, the remainder of which is occupied with experiments on gases, etc., dated August 1804. It is, however, quite possible that the entries in question, which

are reproduced below, are of a different date from this, since the matter contained in them is quite disconnected from that on the preceding pages :—

[i. 287]

Barytes – carbonat	– 53
sulphat	54 (Four.)
nitrat	33
muriat	33
Mur. acid mur. am.	– 8·5
mur. soda	do.
mur. lime	more
Strontian – sulphat	37

[i. 288]

Lime from carb. lime	= 16
from sulph. lime	= 21
from oxalat lime	= 21
from phosph. lime	= 15
Magnesia – oxalat	15
sulphat	16
– carb.	20 ?
Potash – sulph. pot.	30 +
nitrat pot.	20
carb. pot.	14 nearly true ?
mur. pot.	17
Alumine sulph.	18

The numbers have evidently been obtained from the analytical results by calculating to the nearest whole number how much of the base would combine with the amount of acid represented by the atomic weight of the latter.

In most of these cases it has been possible to trace back the numbers to their source, and to find the actual analysis from which the calculation was

made. This will be seen from the following table :—

TABLE C

Substance.	Atomic composition.		Percentage composition.				Author of analysis.
			Theory, calculated from the Atomic Composition.		Found.		
	Base.	Acid.	Base.	Acid.	Base.	Acid.	
Barium carbonate .	53	15	77.9	22.1	78	22	Kirwan
Calcium carbonate .	16	15	51.6	48.4	51.5	48.5	Thomson
Magnesium carbonate .	20	15	57.1	42.9	57	43	Kirwan
Potassium carbonate .	14	15	48.3	51.7	48.8	51.2	Kirwan
Barium sulphate .	54	28	65.9	34.1	66	34	Fourcroy
Calcium sulphate .	21	28	42.9	57.1	43	57	Chenevix
Magnesium sulphate .	16	28	36.4	63.6	36.7	63.3	Kirwan
Calcium oxalate .	21	22	48.8	51.2	48.9	51.1	Bergman
Calcium phosphate .	15	18	45.5	54.5	46	54	Fourcroy
Barium muriate .	33	10	76.7	23.3	76.2	23.8	Kirwan
Potassium muriate .	17	10	63	37	64	36	Kirwan

It will be noticed that the results are incompatible with Richter's "touchstone of analysis," for the combining proportions of lime and baryta vary with each salt from which they are calculated, and do not even stand in the same ratio to one another, as they should do were the analyses correct.

Dalton's next attempts to obtain atomic numbers for the earths were made in 1806. In August of that year the two columns (1) and (2) (Table B) are found, and these are followed in September by a careful comparison of the composition of a large number of salts, the results of which are embodied

in column (3), which was published in the *New System*, part i.

A table of the amount of base combining with one part of acid in the salts of the seven chief bases with the five chief acids was first drawn up from the analyses of Kirwan, Chenevix, and others; the atomic weights were then calculated from these numbers assuming the atomic weight of the acids, a selection made of the most suitable number, and finally a table of composition drawn up, from which the following (Table D) is an extract, more than 40 salts being included in the original.

TABLE D

[ii. 248]—September 1806.

			Theory. Per cent.			
		Acid.	Base.	Acid.	Base.	Kirwan.
Sulphate of soda .	1 to 1	34	28	55	45	56 44
„ of potash .	1 to 1	34	42	45	55 +	45 55
„ of lime .	1 to 1	34	23	60	40 +	59 41
Nitrate of soda .	2 to 1	38	28	57½	42½	57½ 42½
„ of lime .	2 to 1	38	23	62.3	37.7	64½ 35½
Muriate of soda .	1 to 1	23	28	45	55	42 58
Carbonate of soda.	1 to 1	19	28	41	59	40 60
etc. etc.						

The atomic weights of the acids here employed are those of column (7), Table A.

It will be observed that the agreement with the analytical results is by no means perfect. Kirwan's results were, as a matter of fact, inconsistent with one another, as was pointed out by Richter and

afterwards by Wollaston, and there seems reason to suspect that the trouble involved in the examination and arrangement of these faulty results may have been the cause of Dalton's celebrated declaration of independence. "Having been in my progress so often misled by taking for granted the results of others, I have determined to write as little as possible but what I can attest by my own experience."

The experiments which Dalton instituted in accordance with this plan are fully detailed in the *New System*, and require no further discussion here.

VII. THE METALS

In dealing with the constitution of the metallic salts and oxides, and with the atomic weights of the metals, Dalton followed the same lines as he had done in the case of the alkalis and their salts. He first of all made use of the existing analytical material, and selected the atomic weights, which disagreed least with the often inconsistent analyses of the metallic oxides. When new results appeared in the chemical literature of the day they were embodied in these lists, and finally the whole subject was experimentally treated in the manner described in full in the various sections of the *New System*, vol. ii. The numbers adopted for the most important metals at different times are contained in the following table :—

TABLE E

	1	2	3	4	5	6	7	8	9	10
Gold	O = 5.5 105	O = 7	O = 7 140	O = 7 140 - 150	O = 7	O = 7	O = 7	O = 7 140	O = 7 140?	O = 7 60+
Platina	.	.	.	90 - 100	.	.	.	100	100?	73
Silver	105	63	63	100 ±	115	100 ±	100	100	100	90
Mercury	105	124	133 112	.	.	166	166	167	167	167 or 84?
Copper	44	56	56	.	.	56	56	56	56	56 or 28?
Iron .	16	15.3	38 } 19 }	.	29 or 58	40	50	38	50	25
Tin .	22	28	36	70	.	.	50 - 60	.	50	52
Lead	105	52	63	95	106 or 90	95	95	95	95	90
Zinc	22	56	50+	56	52	56	56	56	56	29
Bismuth	22	63	60	117 ±	.	.	62	.	68?	62
Antimony	.	46.3	.	32 - 44	.	.	37? 50? 40	.	40	40
Arsenic	.	21	25 } 50 }	40 - 48	.	.	42?	.	42?	21
Manganese	16	28	56	58?	.	.	63	.	40	25

(1) Notebook, i. 381-2, March 1804.

(2) Calculated from a table in the Notebook [i. 318], compiled in the summer of 1804 (see p. 97).

(3) Notebook, ii. 284, 14th August 1806.

(4) Notebook, ii. 255, September 1806.

(5) Notebook, ii. 247, 16th September 1806.

(6) Notebook, ii. 256, October 22nd, 1806.

(7) Notebook, ii. 421, July 1807.

(8) *New System*, part i. p. 219.(9) *New System*, part ii. p. 546.(10) *New System*, vol. ii. p. 352.

The theory which guided Dalton in his selection of the atomic weight of a metal was that the oxide was most probably composed of one atom of metal to one atom of oxygen, whilst when two oxides existed, the second and higher of the two was composed of one atom of metal to two of oxygen. The very earliest list of numbers (1) is dated March 1804, the numbers being calculated for $O = 5.5$, and taken, as a rule, from very inaccurate analyses.

The numbers in column (2) (Table E) have been calculated from a table found in the Notebook, i. 318. This table contains the composition of twenty-three metallic oxides as found by experiment by various chemists, expressed in the manner shown by the following extract :—

[i. 318]. Theory of oxides of metals :—

1st oxide is 1 metal and 1 oxygen.

2nd oxide is 1 metal and 2 oxygen.

	Expt.		Theory.	
	(1)	(2)	(1)	(2)
5. Copper .	$88\frac{1}{2}$ to $111\frac{1}{2}$	80 to 20	88.9 to 111.1	80 to 20
6. Iron .	73 to 27	52 to 48	68.5 to 31.5	52 to 48
13. Manganese	80 to 20 and 60 to 40	74 to 26	80 to 20 and 57 to 43	66.7 to 33.3

It will be seen that Dalton has been testing the theory placed at the head of the page, by assuming that the experimental composition of one of the oxides of each metal was correct, and calculating that of the other according to his theory.

All the analyses quoted in this table are to be

found in Thomson's *System of Chemistry*, 2nd edition, 1804.

The numbers in columns (3) and (6), Table E, are taken from short accounts of the metals in question jotted down in the Notebook. Those of earlier date are almost unaccompanied by analytical data, whilst the later ones contain an elaborate list of the analyses which had at that time been published ; those of Wenzel, Bergman, Klaproth, Morveau, Berthollet, Pelletier, Kirwan, Lavoisier, Proust, and others, being quoted. It was only after 1807 that Dalton's own analytical researches on the composition of the metallic salts were instituted, and in this difficult branch of practical work, begun at so late a period in his life, he never attained any great skill. The revolution in chemical analysis which was inaugurated by the work of Klaproth, Berzelius, Rose, and Proust, soon raised the standard of accuracy far above that to which Dalton had attained, and his work in this respect must be classed with that of the old school rather than the new.

CHAPTER IV

DALTON'S LECTURE NOTES

*Notes of Lectures delivered at Royal Institution in
London December and January 1810*

Lecture 15.—ON HEAT

23rd January 1810.—The very general importance of facts and experiments relating to heat will be admitted by all who are acquainted with the mechanical arts and with physical science. Facts and experiments, however, relating to any subject, are never duly appreciated till, in the hand of some skilful observer, they are made the foundation of a theory by which we are able to predict the results and foresee the consequences of certain other operations which were never before undertaken. Thus a plodding experimentalist of the present time, in pursuit of the law of gravitation, might have been digging half-way to the centre of the earth in order to find the variation of gravity there, were it not that the sublime speculations of Newton have already anticipated the result, and

spared him the undertaking of a fruitless and endless labour.

In reference to the subject before us, it has been found that if a quantity of any elastic fluid be compressed by *mechanical* force, its temperature is raised, or it parts with a quantity of its heat — and it recovers the same quantity of heat again upon being liberated, and the same volume as it previously possessed. This is a particular fact. Again, it has been found that a piece of iron may be hammered till it is red-hot; that it is condensed in volume by the operation; and that it does not, like the air, recover its former heat and former volume of its own accord, but requires to be heated red-hot again and cooled slowly before it resumes its original temperament and volume. This is another fact. But of how much more importance would it be to ascertain from these and such like facts that it is an universal law in nature that whenever a body is *compressed*, whether by *mechanical* or *chemical* agency, it loses a portion of its heat; and whenever a body is *dilated* it *gains* a portion of heat from other bodies?

Now, whether this is in reality a law of nature is not yet, perhaps, clearly ascertained; but this is certain that a person apprehending such a law is more likely to have a proper bent given to his investigations than one who makes a number of experiments without any fixed object in view.

I have made these observations to shew that,

however guarded we should be, not to let a theory or hypothesis, contradicted by experiment, mislead us ; yet it is highly expedient to form some previous notion of the objects we are about, in order to direct us into some train of enquiry.

The doctrine of heat is justly considered as constituting a fundamental part of chemical science. It constitutes the basis of mechanical power in that most useful instrument, the steam-engine. The cause of animal heat forms one of the most important enquiries in physiology. Even in the mechanical arts the knowledge of heat is necessary. The clock and watchmakers are not competent to their arts if they do not understand the laws of expansion by heat. We have known instances of very large castings of iron having been pulled to pieces by their own reaction, before ever they were cooled, by the careless or injudicious manner of cooling them. And every one knows the nice attention to temperature that is requisite in manufacturing and working with glass.

It would be endless to enumerate the arts, sciences, and manufactures in which a knowledge of the nature and laws of heat is advantageous and even expedient. If the economy of fuel was the only object in pursuit in these speculations it would be well deserving our attention.

The *first* question that naturally arises for our discussion is—

What is Heat?

Were we to proceed as the experimental philosopher must do—that is, in the *analytical* mode of investigation, this question would most properly be the *last*. But as we profess to teach or instruct from the knowledge we have previously acquired, or in the *synthetical* way, this question may properly be considered at the outset.

1. Theory—Heat a distinct and peculiar elastic fluid *sui generis*; its leading features are to be *repulsive* of its own particles; and *attractive* of those of other matter . . . quantity incapable of change.
2. Theory—Heat is a quality of bodies—consists in some kind of vibration of the particles — is, like mechanical forces, communicated from one body to another; is incapable of change in quantity, like the force of elastic bodies.
3. Theory—Heat is a quality of bodies—consists in some kind of vibration of the particles—and is capable of being *generated* or *destroyed*, consequently is capable of change in quantity in different bodies without reciprocal communication.

Animadversions on these theories :—

Refer to diagram.

Refer to a candle burning.

Refer to ordinary combustion.

Refer to the heat of the human body.

Refer to freezing water.

This leads to *capacity* for heat : refer to two equal electric jars, one thick, the other thin ;

And to capacity as applied to the human intellect—thick skull and thin.

Quantity of heat and *intensity* of heat considered : refer to water and mercury. See diagram of capacity.

Whatever theory of heat we adopt we must allow of *quantity* and *intensity* of heat.

Measure of *intensity* or temperature by the thermometer :—

Investigations of De Luc, Crawford, etc., concerning the thermometer.

De Luc finds mean	119°	} instead of 122°.
Crawford .	121°	

Principle wrong that equal weights (or equal bulks) of water mixed at any different temperature should give the mean. Reason assigned. Error, 8° above the mean.

These considerations induced me to try some other method :—

1. Discovery that water and mercury expand by the same law—namely, the expansion as the square of the temperature from the point of greatest density or congelation. See diagrams.

2. That the force of steam is in geometrical progression to equal increases of temperature or *intensity* of heat. Instances in steam of water and ether.
3. That the expansion of air is in geometrical progression to equal increments of temperature.

Animadversions on former experiments on the expansion of gases, General Roi, Morveau, etc. See diagram.

4. Refrigeration of bodies in geometrical progression to equal increments of temperature.

This law, suspected by Newton, but found not to answer by the common thermometer.

Experiment—If a thermometer be heated to 400° above the temperature of the air and suffered to cool, it will be found :—

400°			
200° in 2 minutes of time.			
100	„ 2	„	more.
50	„ 2	„	„
25	„ 2	„	„
$12\frac{1}{2}$	„ 2	„	„ etc. etc.

Here the quantity of heat thrown off in any given time is as the *intensity* or excess of temperature, as it ought to be. Hence the thermometer so graduated must be concluded to be an accurate

measure of *intensity* of heat, or, as it is more frequently called, *temperature*.

The agreement of these four important phenomena in establishing a great fundamental law of heat is such as must carry conviction to every one who will take the trouble duly to consider them—the only doubt that can exist is as to the accuracy of the *facts*. This at present may be said to rest entirely on my authority, though it need not in fact do so. I might appeal to Bétancourt in regard to steam, to General Roi in regard to expansion of air, to Blagden in regard to expansion of water. The experiments on the refrigeration of bodies are more peculiarly mine. They are, however, the most easily made, etc.

It is now one and a half year since these results were before the public. No animadversions on them in this country, notwithstanding their evident importance. Perhaps the repetition of the experiments, and the confirmation of them, may be soon expected from France, etc. If this should be the case we may well exclaim—Where are the *descendants* of *Newton*, of *Bacon*, of *Hooke*, and of *Boyle*, that the merits or demerits of the productions of *Englishmen* cannot be ascertained in their own country? I trust and hope, for the honour of my country, that this *inattention* to new and important views on a subject of so much consequence as that of heat, is somehow or other *accidental* or *apparent only*, and is not to be ascribed to the want

of ardour in the pursuit of science, or to the incompetency of those whom the public look up to as judges and authorities.

Lecture 16.—ON HEAT

24th January 1810.—From the observations made by several gentlemen at the conclusion of last lecture, I apprehend I may have expressed my ideas somewhat incorrectly in some points relative to the quantity of heat which a mercurial or other thermometer receives or parts with in its progressive expansion or contraction, as determined by the new graduation.

Now I would have it understood that I conceive the new graduation of the thermometer to be significant only of the *intensity* of heat in the thermometer, and not of the *quantity*; this last, namely, the *quantity* of heat, I conceive increases with the number of degrees or volume of the mercury, so that a small portion of the heat added goes to increase the capacity of the body for heat, and the rest goes to increase the *intensity*. In the ordinary range of the *mercurial* thermometer—from freezing to boiling water—however, the expansion is so small, and the increase of capacity so trifling, that in a practical point of view we may reckon the increase of *quantity* of heat to hold the same ratio as the increase of the *intensity*, and the quantity of

heat to be expended solely in producing that intensity.

Refer to air thermometer.

In a *water* thermometer, however, this conclusion cannot be admitted. For it is evident, granting the accuracy of the new graduation, that the excess of temperature of 8° , observed upon mixing equal quantities of water of 32° and 212° , can only be accounted for on the supposition that these 8° arise from the superior capacity of water of 212° to water of 32° . I stated the fact in the former lecture that equal quantities of water of the two temperatures just mentioned, on being mixed, give a temperature of 130° on the new scale, instead of 122° , the arithmetical mean. This excess of 8° must then be ascribed to the greater capacity of water in the higher part of the scale.

Refer to the *gradual* expansion of *air*—effect proportional to cause. Something like this in the expansion of solids.

But it has been observed that the law of expansion of liquids exhibits something strange.

Water expands 1 for 1° in one part, and 340 for 1° in another part; and even expands by cold the same as by heat!!

I have attempted a solution of this under the head of *congelation*. Refer to diagrams.

Specific heat of bodies is the numerical relation of the real quantity of heat in *equal weights* or in *equal bulks* of two different bodies.

Thus if the specific heat of a given bulk of water be expressed by 1, that of the same bulk of mercury will be nearly $\frac{1}{2}$. If weights be used instead of bulk : then the relation will be 1 to $\frac{1}{2.5}$ nearly.

Method of ascertaining specific heats :—

Liquids, the glass, globular, suspended with a thermometer. Time marked in cooling—

Solids—by putting them heated into a given volume of water, etc.

Gases—difficult.

Notion of equilibrium of heat :—Dr. Crawford's, Prevost's, on *combined, free, latent*, etc., heat.

Theoretical or speculative views on the heat of gases :—

The principle will perhaps extend to all other bodies.

Heat produced by combustion and chemical mixture.

1st mixture of sulphuric acid and water :—

Mix 1.6 sulphuric acid.

1 — W. gives temperature 260° .

Diminution of capacity about $\frac{1}{16}$.

Refer to diagram, and explain numerically ; also to air bottle by the bye. Ignited wire in hydrogen.

Hence may be inferred that in combustion the like effect is produced.

Difficulty of proof in gases :—

2. Mixture of snow and salt produces cold, attended with some increase of capacity.
3. Nitric acid and lime produces heat. Lavoisier and Laplace found cap. of mixture *increased*. I found it *diminished*, but less in proportion than other bodies.

Combustion of oil, tallow :—

10 grs. heated 2 quarts water 5° .

Hydrogen raises equal vol. W. $4^{\circ}.5$.

Coal gas 10° , etc. See *New System* (p. 77).

Hence infer the large quantity of heat in oxygen gas. Objection refuted.

Ignition in galvanic and electric circuits explained.

Natural zero of temperature or absolute cold.

See diagram.

Suppose a mixture produced 200° of heat, and was found to have lost $\frac{1}{20}$ th of its capacity.

Then the zero would be at 4000° below the temperature.

Radiation of heat :—

Common explanation from diagram.

Heat of common fire radiant.

Leslie's discovery of effect of surfaces. . . .

Glass and paper to metal as 8 to 1.

One of his positions controverted. See Canister.

Comparison of Heat and Electricity and Light

In proportion as we advance in our knowledge relating to light, heat, and electricity, in the same proportion we find *resemblances* amongst them. Solar light and heat are subject to *reflection* and *refraction*: ordinary heat is subject to *reflection*, and can be brought to a focus, like light. *Heat* and *electricity* are alike found in all bodies, and in different *quantities* and *intensities*. Whenever we rob any body of its *electricity*, we must give the same quantity to another; the case is the same with heat. Electricity can be conveyed with a celerity which is perhaps only equalled by the celerity of radiant heat or of light. The principal *visible* effect of electricity in igniting wires is the exhibition of *heat*.

May we not then look forward to the time when these three important agents shall be shown to arise from one and the same principle? And, in the meantime, is it not most consistent to conclude that these agents are of the same nature? If any one of these three, *heat*, *light*, and *electricity* be deemed a *fluid*, then the other two must also be deemed *fluids*. If any one of these be deemed *powers* or *properties*, then all three must be deemed *powers* or *properties* of matter. Now with regard to *light*, our knowledge concerning it remains nearly the same as it was in the time of *Newton*. His decided opinion concerning light was that

of its being a *body*, not a property of other bodies. Experience has added much to our knowledge of heat and electricity since the time of Newton—and from the preceding remarks it should seem that there are many striking features of resemblance amongst the three. May it not then be argued that the notion of heat and electricity being also *bodies*, is more conformable to the Newtonian philosophy than the opposite doctrine, which considers them as mere *qualities* or *properties* of bodies?

Lecture 17, see ante, p. 13.

Lecture 18.—CHEMICAL ELEMENTS

30th January 1810.—In the last lecture we endeavoured to show that matter, though divisible in an *extreme degree*, is nevertheless not *infinitely* divisible. That there must be some point beyond which we cannot go in the division of matter. The existence of these ultimate particles of matter can scarcely be doubted, though they are probably much too small ever to be exhibited by microscopic improvements.

I have chosen the word *atom* to signify these ultimate particles, in preference to *particle*, *molecule*, or any other diminutive term, because I conceive it is much more expressive; it includes in itself the notion of *indivisible*, which the other terms do not. It may perhaps be said that I extend

the application of it too far, when I speak of *compound atoms*; for instance, I call an ultimate particle of *carbonic acid* a *compound atom*. Now, though this atom may be divided, yet it ceases to be carbonic acid, being resolved by such division into charcoal and oxygen. Hence I conceive there is no inconsistency in speaking of compound atoms, and that my meaning cannot be misunderstood.

It has been imagined by some philosophers that all matter, however unlike, is probably the same thing; and that the great variety of its appearances arises from certain powers communicated to it, and from the variety of combinations and arrangements of which it is susceptible. From the notes I borrowed from Newton in the last lecture, this does not appear to have been his idea. Neither is it mine. I should apprehend there are a considerable number of what may be properly called *elementary* principles, which never can be metamorphosed, one into another, by any power we can control. We ought, however, to avail ourselves of every means to reduce the number of bodies or principles of this appearance as much as possible; and after all we may not know what elements are absolutely indecomposable, and what are refractory, because we do not apply the proper means for their reduction.

We have already observed that all *atoms of the same kind*, whether simple or compound, must

necessarily be conceived to be alike in shape, weight, and every other particular.

Figure of simple atoms:—May be globular, or of the 5 regular bodies. Tetrahedron, Hexahedron.

Whatever may be the figure they must be virtually globular or nearly so, from the great quantity of heat surrounding them.

1. Combination of simple atoms constituting compound atoms.

Combinations generally one to one.

2. Manner of finding the relative weights of atoms.

Instance earths and metals—carbonates, sulphates, etc.

3. Arrangement of 3 or more atoms constituting one compound atom.

See water, etc., and nitrat ammonia.

Hexagon—hence perhaps origin of hexagonal crystals.

4. Of water—

	Ox.	Hyd.
Lav.	85	15
	- 5.6 : 1	
corrected	87½	12½
	- 7 : 1	

Why 1 to 1? because neither syn. nor analysis shows any other.

5. Ammonia—

26 azote + 74 hyd = 4.2 to 1
ought to be 30 „ + 70 „ = 5.1 „ 1

Henry with ours,	}	Hence with nit. gas, always
never so low as 26		too much azote, or else
„ so high as 29		right.

6. Compounds of azote and oxygen are 4 or 5 at least.

- | | | |
|---|--|----------------------|
| | Wt. | Diamr. |
| 1. Nitrous gas | 12 | .947 |
| | Davy— 42 to 47 azote | |
| Sp. gr. 1.1—Theory | 42 | 58 oxy. |
| | 48 measures azote—of which 24 remain
by electrification. | |
| | Wt. | |
| 2. Nitrous oxide | 17.2 from Nitrat. am. | |
| | Davy— 61 to 63 azote | |
| Sp. gr. 1.6—Theory | $59\frac{1}{2}$ | $40\frac{1}{2}$ oxy. |
| | Nit. ox. | Hyd. |
| | Decomp. by hyd. 1 measure + 1 gives 1 azote. | |
| 3. Nitric Acid— | | |
| | Cavendish—from 25 to 30 azote | |
| | Davy—29.5 azote | |
| | Az. | Oxy. |
| Sp. gr. 2.4—Theory | 27 | 73 |
| Exhibition of it in elastic form (see Table) :— | | |
| | Oxy. | Nitrous. |
| | 1 took from 1.4 to 2.3. | |
| 4. Oxynitric acid—26.1. | | |
| | 4 oxy. to 1.3 nit. gives 1 oxy. + 1.3 nitrous. | |
| 5. Nitrous acid—31.2. | | |
| | 1 meas. oxy. takes 3.6 nitrous in water. | |
| | 1 meas. oxy. to 3.6 nitrous gas in a tumbler glass
form nitrous acid. | |

This acid gives out nitrous gas when combining.

Remarks on nitric acid :—

See Table on Board.

2 to 1 strongest acid exhibited.

1 „ 1—very strong.

1 „ 2—boiling point 248° Max.

1 „ 3—nothing remarkable.

1 „ 4—acid of easiest freezing (Cavendish).

Lecture 19.—CHEMICAL ELEMENTS

31st January 1810.—In the preceding investigations on the number and weights of the elementary principles constituting *water*, *ammonia*, and the various compounds of azote and oxygen, you will have remarked that the conclusions were derived principally from the facts and experience of others, without any additional facts of my own discovery that merit particular notice.

The composition and decomposition of water had been ascertained by British and Foreign chemists; that of ammonia by Berthollet and several others; the compounds of azote and oxygen had been successively developed by Cavendish, Priestley, Davy, and others. I may, however, observe that the *nitrous compounds* have occupied a great portion of my time and attention at different seasons. The elegant and instructive experiments on the effect of electricity on nitrous gas deserve notice. By electrifying nitrous gas over water, in a short time 100 measures are reduced to 24, which, upon examination, are pure azote.

1. Theory of it explained.
2. Theory of the formation of nitric acid in Mr. C.'s experiments.

The simple and easy method of combining the *least* portion of oxygen with the *greatest* of nitrous gas, which I pointed out in the last lecture, was the result of my own investigation, and affords a

convincing proof of the real nature of what is called *nitrous acid*, which is constituted of 1 atom of oxygen united to 2 of nitrous gas. (See figure.)

From the preceding remarks it will be perceived that I advanced thus far in my theoretic progress without meeting with much obstruction. The way had been paved by others. But when I directed my views to the compounds of charcoal and oxygen, and charcoal and hydrogen, I found that all the then commonly received doctrines were adverse to my proceeding, and irreconcilable with my views.

Mr. Tennant's experiments in the *Philosophical Transactions*, 1797, had shown the identity of diamond and charcoal in a chemical point of view, but the succeeding experiments of Guyton Morveau on the combustion of diamond supplanted the former in the judgment of great part of our chemists. Diamond was concluded to be a simple body, and charcoal the oxide of diamond. Mr. Cruikshank soon after discovered the gas called carbonic oxide. The doctrine of the compounds of charcoal, or rather diamond and oxygen, then stood thus :—

Diamond	.	.	18 parts.
Oxy.	.	.	10 „
			28 charcoal.
Oxy.	.	.	41
			69 carbonic oxide.
Oxy.	.	.	31
			100 carbonic acid.

A very little reflection convinced me that the doctrine of charcoal being an oxide of diamond was highly improbable—and experience confirmed the truth of Lavoisier's conclusion that 28 parts charcoal + 72 oxygen constituted carbonic acid; also that carbonic oxide contained just half the oxygen that carbonic acid does, which indeed had been determined by Clement and Desormes, two French chemists, who had not, however, taken notice of this remarkable result. Carbonic oxide, being lighter, is the more simple.

$$\begin{array}{l} \text{Hence } 28 + 36 = \text{carb. ox.} \\ \quad \quad \quad + 36 = \text{carb. acid} \end{array} \quad \left. \vphantom{\begin{array}{l} 28 + 36 = \text{carb. ox.} \\ + 36 = \text{carb. acid} \end{array}} \right\} \text{hence } \left\{ \begin{array}{l} 5.4 + 7 = 12.4 \\ \quad \quad + 7 = 19.4 \end{array} \right.$$

Hence carb. acid = 19 as supposed in last lecture.

$$\begin{array}{rcc} & & \text{carb.} \\ & & \text{c. ox.} \quad \text{ox.} \quad \text{acid.} \\ 100 - 47 - 94 \end{array}$$

2. Charcoal and hydrogen :—

Generally mixtures, etc.

Berthollet's late paper; remarks.

Species—(1) Olefiant gas.

100—take 300 oxy.—gives 200 acid.

Exp. by electr., 200.

By 200 forms carb. oxide, 200.

(2) Carburetted hydrogen—coal gas.

100—take 200 oxy.—gives 100 acid.

Exp. by electr., 200.

By 100 oxy. gives 200.

All these prove charcoal to be 5.

Hyd. flame red pale.

Carb. oxide blue.

Carb. hyd. white, like a candle.

Olefiant g. very brilliant white.

3. Sulphur. Wt. 13¹ found from the acids :—

1. Sulphurous oxide.

2. Sulphurous acid.

3. Sulphuric acid.

Boiling point of strongest 620°, contains 81 per cent.

Common acid contains 79, boils 590°.

Remark on Kirwan's table.

Freezing acid - 1.78 - 1 + 2 water - 435°.

Theory—Clement and Desormes, Nicholson, 17.

Sulphuretted hyd., 1 + 1.

My book wrong.² Burned gives sulphurous acid and water.

4. Phosphorus :—

Phosphorous acid.

Phosphoric acid.

Phosphuretted hyd.

5. Alkalies and earths :—

Hydrate of lime.

6. Metals.

7. Metallic oxides.

8. Metallic sulphurets :—

Mr. Hatchett's paper on mag. pyrites gives the 2nd, 3rd, and 5th of iron.

Lecture 20.—CHEMICAL ELEMENTS

3rd February 1810. — When we consider the very important part which the two elements of *hydrogen* and *oxygen* seem to perform in the arrangements of chemical compounds, we are inclined to

¹ The several numbers for sulphur adopted by Dalton are found in Table A, p. 83.

² Sulphuretted hydrogen is given in part i. of *New System* as 1 of sulphur to 3 of hydrogen.

wonder that no more than *one* compound of these two elements themselves should be found.

Water, that most beneficial and essential of all liquids, is formed of hydrogen and oxygen. Besides this one, there is not a compound of these two elements generally known and recognised as such. It is singular if we have not somewhere a principle consisting of *two* atoms of oxygen and *one* of hydrogen; or *two* of hydrogen and *one* of oxygen. The former of these ought to be an *acid*, conformably to what we observe in other similar cases. The latter ought to be a combustible gas. All the other common elements, *azote*, *charcoal*, *sulphur*, and *phosphorus*, combine, each one with two atoms of oxygen, to form acids. Why should not hydrogen do the same? This question has been frequently put, but no satisfactory answer has been given. Upon comparing the results of experience, and applying the theoretic views which I have been endeavouring to develop, it appears to me *very probable* at least that the acids denominated *fluoric* and *muriatic*, with their derivatives, are constituted of the elements of hydrogen and oxygen, and are in reality the very compounds of which we have just been hinting.

I would not, however, be understood to mean that these views are the necessary results of the atomic theory; and that its truth or falsehood depends upon the determination of the question. From the want and imperfection of facts relating to

these subjects, nothing perhaps decisive can be yet advanced. I intend to point out such reasons and such facts as have induced me to adopt the opinion, and must leave it to others to judge how far they support the probabilities above mentioned.

1. Fluoric acid:—

1. Fluoric acid gas from fluate of lime
—a gas combined with flint—*superflu-
ate of silica*. Very heavy gas.
2. No steam in this or muriatic acid
gas; proved from no condensation
by cold, etc.
3. 50 grains fluate of lime gave 75
sulphate, mean between Richter
and Scheele. Hence 15 acid + 23
lime = fluate of lime.
4. Mr. Davy finds potassium burn in
this gas; some hyd. is given out
and fluate of potash formed.
5. Hence 15 being the weight—2 oxy.
+ 1 hyd., etc.

2. Muriatic acid:—

1. Does not contain steam.
2. Mr. Davy finds potassium to burn in
this gas, give hydrogen, and form
muriate of potash.
3. Its weight is $22 = 1$ hydro. + 3 oxygen.
4. Liquid muriatic acid. 1 and 20
water boils at 232° . See diagram.

3. Oxymuriatic acid :—

1. Gas has sp. gr., 2.34.
2. Mr. Davy and the French chemists seem to think this is the simple and mur. acid the compound. Burns with carbonic oxide, etc.
3. The effect of light on a mixt. of this and hydrogen.

4. Hyperoxymuriatic acid :—

1. Consists of 1 oxy. mur. acid + 5 oxygen, 1 hyd. + 9 oxygen.

5. Acetic acid.

Neutral salts :—

1. Carbonates.
2. Sulphates.
3. Nitrates.
4. Muriates.
5. Acetates.

6. Metallic salts :—

Corrosive sublimate. See diagram.

Action of common electricity on compound gases and gaseous mixtures :—

1. No effect on the simple gases hyd., azote, oxy.
2. Ammonia. Decomposed rapidly.
3. Carbonic acid. Decomp. into carbonic oxide and oxygen. Recomposed again.

4. Ether and alcoholic vapour decomposed.
5. Nitrous gas and nitrous oxide. Decomposed.
6. Compounds of charcoal and hydrogen. Decomposed.
7. Compounds of sulphur and phosphorus with hydrogen. Decomposed.
8. Mixt. of any combustible gas and oxygen, new combinations, quick or slow. Generally more rapid than the former.

Difficulty of forming any theory.

Conclusion of the course.

I cannot conclude this course of lectures without expressing my high satisfaction with the general attention that has been given to the subjects under discussion and with the indulgence which has been given me when adverse circumstances occurred. I shall always associate these grateful impressions with the recollection of the event. To those who feel highly interested themselves in the promotion and extension of science, it is a peculiar satisfaction to meet with others of the same description. I shall now return to comparative retirement, in order to prosecute the train of enquiry and investigation which I have briefly developed in the late lectures; the results, I am

confident, will be found of importance ; and will contribute to establish that beautiful and simple theory of chemical synthesis and analysis which I have adopted from a conviction of its application to the general phenomena of chemistry, and which will in due time, I am persuaded, be made the basis of all chemical reasoning respecting the absolute *quantities* and the *proportions* of all elementary principles, whether simple or compound.

R. I. 3rd February 1810.

Then follow in Dalton's handwriting the following extracts from Newton's *Principia*.

[1]. Newton. Query 31.

"The parts of all homogeneous hard bodies which fully touch one another, stick together very strongly. And for explaining how this may be, some have invented hooked atoms, which is begging the question ; and others tell us that bodies are glued together by *rest*—that is, by an occult quality, or rather by nothing ; and others that they stick together by conspiring motions—that is, by relative rest among themselves. I had rather infer from their cohesion that their particles attract one another by some force, which in immediate contact is exceeding strong, at small distances performs the chemical operations above mentioned, and reaches not far from the particles with any sensible effort."

"All bodies seem to be composed of hard

particles." "Even the rays of light seem to be *hard* bodies," "and how such very hard particles which are only laid together and touch only in a few points, can stick together, and that so firmly as they do, without the assistance of something which causes them to be attracted or pressed towards one another, is very difficult to conceive."

"It seems probable to me that God in the beginning formed matter in *solid, massy, hard, impenetrable, movable* particles, of such *sizes* and *figures*, and with such other *properties*, and in such proportion to space as most conduced to the end for which he formed them; and that these primitive particles being solids, are incomparably harder than any porous bodies compounded of them; even so very hard as never to wear or break in pieces; no ordinary power being able to divide what God Himself made *One*, in the first creation. While the particles continue entire they may compose bodies of one and the same nature and texture in all ages; but should they wear away or break in pieces, the nature of things depending on them would be changed. Water and earth, composed of old worn particles and fragments of particles, would not be of the same nature and texture now, with water and earth composed of *entire* particles in the beginning. And therefore that nature may be lasting, the changes of corporeal things are to be placed only in the various *separations* and new *associations*, and

motions of these permanent particles ; compound bodies being apt to break, not in the midst of solid particles, but where those particles are laid together, and only touch in a few points. . . .”¹

[2]. Again, “. . . God is able to create particles of matter of several *sizes* and *figures*, and in several proportions to the space they occupy, and perhaps of different *densities* and forces. . . . At least I see nothing of contradiction in all this. . . .”

Again, “Now by the help of these principles, all material things seem to have been composed of the *hard* and *solid* particles above mentioned, variously associated, in the first creation, by the counsel of an intelligent agent. . . .”

Newton, Prop. 23, B. 2.

“If the density of a fluid, composed of particles mutually repulsive, be as the compression, the repulsive powers of the particles are reciprocally proportional to the distances of their centres. And, *vice versa*, particles endued with such forces will compose an elastic fluid, the density of which is as the compression.”

LECTURES ON NATURAL PHILOSOPHY, ETC.

Introduction

20th April 1814.—It is scarcely necessary, I should think, to insist at large upon the importance and general utility of the sciences usually compre-

¹ Horsley's *Newton*, vol. iv, p. 260.

hended in a Course of Natural Philosophy and Chemistry.

In this country, where the arts and sciences are more generally cultivated than in any other, and to which circumstance, it is allowed, we owe in some degree our present pre-eminence, there cannot be wanting any powerful stimulus to excite the attention to subjects of this nature.

The sciences of Mechanics and Chemistry, taken in their largest acceptation, are certainly the most generally interesting to us in the present state of civilised society. In the large sense of the word mechanics must be considered as comprehending hydrostatics, hydrodynamics, and pneumatics. The many important inventions and improvements in modern machinery are derived from principles which it is the object of these sciences to explain.

Several of the arts depend upon chemistry ; and as the knowledge of chemistry is daily improving, so must that of the arts.

The truly noble and sublime science of astronomy is more than any other adapted to enlarge and expand the mind ; but besides this, an acquaintance with it is essential to the practice of navigation, an art of primary consideration to a commercial and insular people.

Optics, that most curious and highly useful science, the favourite one of our immortal Newton, has lately received considerable improvements from the investigations of various philosophers.

LECTURES ON MECHANICS, ETC.

Introduction

20th April 1818.—It will be universally allowed that the cultivation of mechanical science, in the present state of society more especially, is an object of primary importance. Agriculture, the arts and manufactures, are all interested in the science. It would seem to follow that it is the duty of every one to make himself acquainted with the *first principles* of the science; and it certainly is the duty and interest of those who are actively employed in mechanical occupations, or in the superintendence of such concerns, to acquire a knowledge of the principles more in detail, according to the branch of science which may be more immediately the object of their attention.

The Ancients knew little of mechanics as a science. Galileo, who lived about two centuries ago, may be considered as the father of the modern science of mechanics. Since his time many celebrated mathematicians in different countries have distinguished themselves on this subject; the names of Newton, Leibnitz, the Bernoullis, are well known as originals in this department of science: but it would be unfair to mention a few names only, where so many are entitled to honourable distinction. In the progress of the science a controversy arose, which was carried on with great

warmth and even animosity ; and though it has now been discussed for more than a century, modern writers on mechanics are far from being unanimous on the subject. It related chiefly to the *measure of force* in moving bodies. One party maintained that the force of a body in motion is in direct proportion to its velocity ; the other party contended that the force is in proportion to the *square* of the velocity. According to the former, a body moving with *twice* the velocity has *twice* the force ; according to the other it has *four* times the force. The dispute is evidently one of great importance to the science, as our estimate of the quantity of moving force in bodies must be materially influenced as we adopt the one or the other of these conclusions.

We shall have occasion to advert to this subject more particularly in the second part of mechanics, or that branch called dynamics ; in the meantime I may observe that those who wish to obtain information on this head will find an excellent disquisition on *moving force* in the second volume (new series) of the *Manchester Memoirs*, which I consider as the best essay that has appeared on the subject, and which in my opinion is completely decisive of the controversy. Though in the above-mentioned essay the force of moving bodies is determined to be as the *square* of the velocity, yet the author has shown that the advocates of both sides have taken partial views of the phenomena, and hence he in

some measure accounts for the continuance of the dispute. In the collision of bodies two things always happen, a change of motion and a change of figure ; the circumstances attending the former have always been minutely observed, but those attending the latter have frequently been overlooked, and sometimes the fact itself discarded under the idea of the bodies being *perfectly hard*, as it is termed. But no such idea can be admitted as deducible from observation.

Another unfortunate circumstance has been the consideration that moving force is generated by pressure acting for a *certain time*, whereas it ought rather to be considered as arising from pressure acting through a *certain space*.

But we shall not pursue the subject farther at present.

From the preceding observations it may be inferred that our systems of mechanics are as yet in an imperfect state. Many authors in our own language, as well as in others, have compiled systems which contain important principles and judicious illustrations; but they are all more or less defective in regard to one principal object—namely, the application of *moving force* to the various exigencies of practical mechanics, and particularly so in the estimation of its *quantity* or *measure*.

A good treatise on the elements of mechanics is therefore still a *desideratum* in science.

CHAPTER V

LETTERS WRITTEN AND RECEIVED BY DALTON

Dr. T. C. Hope to Dalton

DEAR SIR—Since I had the pleasure of conversing with you in Manchester, I have thought a good deal upon the subject of your speculations. I cannot say that I am more disposed to agree with you in them, though indeed some things that seemed to be strong objections now appear less decisive, and the whole pleases me with its ingenuity.

I made the following experiment, and I beg you will tell me how far you think it accords with your theory :—

I took two bottles nearly of the capacity of 3xii, I filled one with carbonic acid gas and the other with hydrogen gas, and holding the latter inverted and perpendicular over the former, I connected them by a tube filled with hydrogen gas 4 inches long and between $\frac{1}{5}$ and $\frac{1}{6}$ of an inch in diameter.

In this situation I left them for an hour,

presuming that, as each gas had an elasticity = 30 inches of φ , in that period, and probably in a much shorter, a mutual exchange of half of the contents of each would take place, provided the theory were true. The result was that a quantity of carbonic acid gas = $1\frac{1}{2}$ oz. m. had entered the bottle containing hydrogen, ascertained by observing the amount of the absorption occasioned by lime-water, and an equal bulk of hydrogen had descended into the carbonic acid determined by the amount of unabsorbed residuum after washing with lime-water.

Suppose a bottle were filled with sand and the atmospheric air were extracted from the interstitial spaces by an air-pump, and a communication then established between the interior of this bottle and a bottle either of hydrogen or carbonic acid gas. Don't you imagine that in much less than an hour, that in a few seconds, the gas would make its way between the particles of the sand, though the interstices between them must be incomparably smaller than those between the particles of another gas?

In our last conversation you mentioned that you had ascertained that water does not expand as its temperature sinks from 40° to 32° . Would you be so obliging as state to me the data on which you form your opinion?

Would you also communicate to me the other very interesting positions respecting heat which you read to me?

I see from Mr. Henry's paper that he is disposed to adopt your opinion that elastic fluids are absorbed by, or rather enter into liquids, upon the same principles elastic fluids mix together. Will this apply to those cases in which water absorbs many times its own bulk?

As in the course of my lectures which I have just begun I shall have *very* soon occasion to speak on these subjects, I should be glad how soon you favoured me with a letter in reply.—I am, dear sir, your very obedient servant,

THOS. CHAS. HOPE.

EDINBURGH, 4th November 1803.

NOTE

The argument advanced by Hope against Dalton's theory of mixed gases is combated by the latter in the *New System*, vol. i. pp. 175-6. The idea that the interstices between the particles of sand must be incomparably smaller than those between the particles of a gas is interesting in view of the estimate arrived at from the molecular theory of gases that 1 cb. c. of air contains about 21 trillions of molecules.

In the *New System*, p. 426, Dalton shows that the absorption of ammonia depends on the pressure of ammonia above the liquid, in just the same way as the absorption of any gas depends on the pressure of *that* gas on the liquid.

Dr. T. C. Hope to Dalton

Dear Sir—I have availed myself of all the time you allowed me before you should expect a reply to your very acceptable letter of 8th November. In this period I have had occasion to peruse your various papers in *Manchester Memoirs*, and to consider them with mature attention. I have been greatly pleased with their ingenuity, and delighted with some of the general principles which you have established.

I cannot say, however, that yet I agree with you in some of them, and the constitution of mixed gases is one of the hypotheses to which I cannot subscribe. With regard to the experiments of which you mention you had lately presented an account to the Society similar to the one I detailed, I must express my concurrence in the sentiment that “The effects being alike in the different cases, are to be ascribed to the same cause.” Now, you mention that the appearances exhibited by oxygen and nitrous gas did not differ from those arising from other gases. Between the former the action is unquestionably chemical, and countenances the opinion that that of the others may be of a similar nature. I confess, however, that I have difficulty in applying this to the case of oxygen and hydrogen, which I presume you likewise tried. For if chemical attraction were

here exerted, there should be condensation and production of water.

The reason you assign for the slow intermixture of the two gases affords what I conceive the strongest objection to the theory in general. You impute it to the operation of the atmospheres of caloric surrounding the particles of the different gases. This atmosphere I deem the essential cause of the elasticity and repulsion among the particles of the gas, and I cannot conceive that this atmosphere as it surrounds a particle of oxygen should repel the atmosphere that surrounds another particle of oxygen and should not repel the atmosphere that envelopes a particle of azote, hydrogen, or any other gas.

I shall, with much impatience, expect the establishment of the general law of expansion of fluids which you announce to me. I imagine, however, you must make an exception in the case of water, on account of its peculiarity of constitution. From the interesting experiments you hinted, when I had the pleasure of conversing with you, and from the differences you notice as occurring *apparently* in the volumes of this fluid according to the nature of the material of the apparatus, you may perhaps imagine I am claiming an exemption in favour of water to which it is not entitled. Mr. Hutchinson indeed yesterday gave me a short account of your late communication, which from his account

appears to bear the same stamp of ingenuity which so strongly characterises your former papers. When I was preparing to lecture on the motions produced among the particles of fluids, I foresaw that your refutation of the supposed peculiarity would throw a great many fine pieces of reasoning respecting its importance in the economy of nature, etc., into the greatest confusion. I was determined, therefore, to satisfy myself by actual experiment, but in a manner which I should conceive to be free from every objection at least arising from the influence of the vessel. I made the experiment and convinced myself that the supposed law is a real and true one. I hope you will excuse me for having announced in my lectures the grounds on which you denied its existence, having mentioned them in those terms of respect, in which I speak of all your speculations. That notice I deemed an essential preamble to the statement of my own experiments.

The outline of my experiments is :—Take a tall jar full of ice-cold water, have a thermometer near bottom and near surface, place in a warm room. Bottom gains temperature soonest, and rises quickest to $39\frac{1}{2}^{\circ}$, then top equals and afterwards gains temperature fastest. Take same jar full of water at 50° , surrounded with water of 32° or ice and water. Bottom cools quickest till it comes to 40° —then equality prevails, and below 40° top

cools quickest. Take a tall jar full of water at 50° , surround a few inches of top (by due contrivance) with freezing mixture. Bottom cools quickest to 40° or $39\frac{1}{2}^{\circ}$, then is stationary for any time, while top cools quickly to 32° and freezes.

Take tall jar with water 40° and place a few inches of bottom in freezing mixture. Top cools at first fastest, then nearly at same rate with bottom till 32° , when congelation around sides of glass takes place. Mr. Hutchinson witnessed one of the experiments. I know not whether they will seem as decisive to you as they do to me.

I have hunted the different public and private libraries for *Gren* but in vain. Lord Glenlee has a copy of it, but unluckily it is sixty miles off. If you can't get the information you desire else . . .

Dr. T. C. Hope to Dalton

Dear Sir—Above a month has elapsed since I wrote you, but my letter from foolish negligence was never sent to the post office.

While in London I had no thoughts of interrupting those occupations in which you must have been incessantly engaged, by renewing any controversial discussion.

Since I heard from you I multiplied and varied my experiments, and had so uniform results that, in spite of your friendly caution, I ventured

to read the detail of them to the Royal Society of this place. My object was to prove that there really does exist the supposed peculiarity in the constitution of water in regard to the effects of heat upon its volume. It seems, therefore, to me very strange that that fluid, that has suggested your general law of expansion, should be an exception to it.

As I am persuaded that you have not hastily concluded that the common notion is erroneous, and that you have proceeded on the support of ingenious experiments, I am very anxious to learn the particulars of those which have decided your opinion. Mr. Hutchinson communicated to me a general outline of them.

Shall they soon be published, or could I by any means have a perusal of them?

A principal reason for my eagerness on this point is, that I shall be determined in all probability as to the printing of my paper by what you shall do. If you publish, from the great weight which your well-merited reputation gives you with the scientific world, I shall feel myself called upon to defend a truth which I conceive I have established. If you do not mean to communicate your experiments to the world, mine may also remain unknown, seeing that they only go to determine a matter of fact, of which at present no doubt is in general entertained.

Want of time prevents me from saying any-

thing at present respecting the other points on which we differ. Those which are purely speculative will long afford room for discussion. Respecting a matter of fact, which can easily come under the test of experiment, we cannot be long at variance.

Wishing you every success in your investigations.—I am, dear sir, your most obedient servant,

THO. CHAS. HOPE.

EDINBURGH, 29th March 1804.

Dr. T. C. Hope to Dalton

9th August 1804.

Dear Sir—Undismayed by the caution you gave me, I have ventured to put to the press my sentiments on the *contraction of water by heat*. After the permission you gave me to state your sentiments and the curious experiments upon which you grounded your opposition to the general opinion as the circumstances which called forth my attention to the subject, I hope I have not exceeded the bounds of that leave in introducing the enclosed paragraph into my paper. I expect in a few days to have the pleasure of transmitting the paper itself, and shall then be impatient to learn whether my experiments make any impression on you. I beg you will let the note addressed to our friend reach him.—I am, dear sir, your obedient servant,

THO. CHAS. HOPE.

NOTE

Dalton's views as to the temperature of greatest density of water are fully explained in the *New System*, pp. 22-35. The experiments to which Hope refers (Royal Society, Edinburgh (1805), 5, 379) were carried out in the early part of 1803.

Dalton perceived that when a liquid is heated in a vessel there may be an apparent point of greatest density, due to the fact that whilst the vessel expands almost equally for equal intervals of temperature, the liquid expands more as the temperature rises (according to his own view in proportion to the square of the temperature above that of the greatest density). Hence if the absolute expansion of the liquid at any temperature is less than that of the vessel, an apparent contraction will occur, whilst as the temperature rises the expansion of the liquid will increase and finally become greater than that of the vessel.

By observing the apparent temperature of greatest density in vessels made of different materials, and allowing for the expansion of these materials, the actual temperature of greatest density can of course be calculated, and Dalton seems to have concluded from his early experiments that this actual temperature was that of the freezing point, the calculated and observed apparent temperatures agreeing very well, as shown below, especially in the case of lead.

[Notebook, vol. i. p. 177]. 20th May 1803.—“*N.B.* Water may be stated to expand $\frac{1}{23}$ from F. to B., allowing for glass.

Glass should by this be $\frac{1}{184} = 42^\circ$.

Lead by Smeaton is $\frac{1}{118}$. This gives 50° for the stationary point.”

[P. 186]. “29th June 1803.—Large lead vessel. (A cooling mixture.)

$$45^\circ = 160$$

$$46 = 150$$

$$48 + = 130$$

$$49\frac{1}{2} = 127$$

$$50\frac{1}{2} = 126$$

$$51\frac{1}{2} = 127$$

$$53 = 130$$

$$53\frac{1}{2} = 135$$

It appears that $50^\circ\frac{1}{2}$ is the lowest point of lead.”

Hope's celebrated experiment was independent of the expansion of the vessel, and we find Dalton in the *New System* admitting the existence of a maximum density above the freezing point. His own observations, however, as there recorded, led him to place it at 36° , instead of 39.5° , as determined by Hope. The mean of the most accurate modern determinations is $39^\circ.27$ F. ($4^\circ.04$ C.)

Dr. T. C. Hope to Dalton

Dear Sir—I shall have much pleasure in seeing you in Edinburgh and forwarding, so far as lies in my power, your scheme of a short course of lectures.

I cannot, however, form any reasonable con-

jecture respecting the probability of a numerous audience. The number of students that enter into the more difficult discussions upon the subject of your speculations is by no means large, and there are not many gentlemen unconnected with the university who are sufficiently conversant with these subjects to take a deep interest in them. I do not state these circumstances by any means to start any obstacle to your plan, but to prepare you for being satisfied with a moderate number of hearers.

In case you put your intentions in execution, the sooner you come to Edinburgh the better, as after the beginning of April the students begin to desert.—I am, sir, your most obedient servant,

THO. CHAS. HOPE.

EDINBURGH, 6th March 1807.

T. Thomson to Dalton

Dear Sir—I have just received your letter, and think that the course of lectures which you propose to give here will be highly grateful to all the true lovers of philosophical chemistry. It is impossible to foretell the degree of success which you will meet with here. Indeed that will depend in some measure upon the exertions of your friends. I shall do everything in my power to promote your success, both by mentioning your plan in my class and by recommending it privately to my

friends, and if there be anything of which you may stand in need and which I can supply, you may freely command it. I do not know what place you may pitch upon for giving your lectures, but if you are unprovided and if my class-room will answer your purpose, I shall give you the use of it with much pleasure. I have given a pretty detailed account of your theory of atoms in my new edition not yet published; but it is very possible that it differs from your conclusions in many particulars.

It may perhaps be worth your while to consider with yourself and to consult your friends whether it would not be better to extend your lectures to twelve or so and to charge a guinea, instead of half a guinea. You would be thus enabled to do justice to your subject, and the profit would be the same.—I am, dear sir, yours sincerely,

THOMAS THOMSON.

EDINBURGH, 8th March 1807.

I hope Mr. William Henry, whom we had the pleasure of seeing here some time ago, has not been the worse for his winter journey. I can give you very little chemical news from Edinburgh. But when you come you will see what we are doing. I have to thank Mr. Henry for the use of his paper on Urinary Calculi, which I have not yet returned, because in a few weeks I shall

be at that part of my new edition and wish to have it by me. I have also received from him a piece of zinc wire sent by I do not know what gentleman. Might I beg the favour of you to present him my respects, and to let him know that I have got these things, and that I am much obliged to him for his attention.

W. Allen, F.R.S., to Dalton

LONDON, 7th of 2nd month 1809.

Respected Friend—I received thy interesting letter, and to begin with the first subject in it the present price of quicksilver is 5s. 4d. With respect to thy experiment in which only from 4 to 5 per cent of carbonic acid was found in the expired, thou wilt find by reference to the paper that we obtained about 5 per cent in that which was pushed off from the mouth into a eudiometer, but it is to be remarked that in this case the air proceeding from the vesicles in the lungs gets mixed with the air in the fauces and mouth which has never entered that organ, hence there is great difference between a *short* and a *long* expiration. The subject of aqueous vapour is reserved for our next communication; we did not intentionally omit the name of Crawford, but shall probably have occasion to notice him in our subsequent reports on this subject. We have made no further experiments on the absorption by charcoal than those detailed in the

transactions, which appear fully to warrant the inference drawn from them.

We can only say with respect to our eudiometer that its results are beautifully uniform, and that it is managed with less difficulty than any other. We conceive there is a strong objection to the use of nitrous gas on divers accounts ; in the first place, it is very liable to contain a mixture of azote or nitrous oxide ; and in the next place, it would be very troublesome to be obliged to examine your nitrous gas for this, whereas in our method we know that the green sulphate will not take up any azote, and consequently this source of error is avoided, and any nitrous gas which might have mixed with the air under examination is readily taken out by a simple solution of green sulphate.

I intend to keep a look out for Attwood upon motion, but it is now very scarce, and only to be picked up by chance.

Davy thinks he has proved azote to be a compound of oxygen and hydrogen ; for having caused potassium to absorb a considerable quantity of ammonical gas he procured scarcely anything but hydrogen from it, and a considerable portion of potash was found. Some of his late experiments have led him to query whether oxygen and hydrogen are not water combined with the electric fluid in a peculiar way. If this should be established, the foundation of the Lavoisierian theory is removed. Present me kindly to Henry, and tell him that I

fully purpose to attend at his election and put in my ball for him, though it will be no otherwise necessary than as a testimony of friendship.

Requesting to hear from thee when convenient.
—I remain, thine sincerely, W. ALLEN.

NOTE

The papers to which reference is made are (1) "On the Changes produced in Atmospheric Air and Oxygen Gas by Respiration," by Allen and Pepys (*Philosophical Transactions*, 1808, p. 249), and (2) "On Respiration," Allen and Pepys (*Philosophical Transactions*, 1809, p. 404).

The oxygen in the expired air was determined by treating it first with a solution of nitrous gas in green vitriol and then with a solution of green vitriol, a process proposed by Davy. Since the nitrous gas prepared from copper by nitric acid always contains nitrogen and nitrous oxide, this process was an undoubted improvement upon the old one.

Davy's experiments on ammonia are to be found in the Bakerian lecture for 1808, and an appendix to it, read 2nd February 1809 (*Philosophical Transactions*, 1809).

The experiments on charcoal are to be found in a paper "On the Quantity of Carbon in Carbonic Acid," etc., by Allen and Pepys (*Philosophical Transactions*, 1807, p. 267).

T. Thomson to Dalton

EDINBURGH, 13th November 1809.

Dear Sir—I have been looking for some time for the second volume of your chemical work, the period at which you had promised to publish it having long elapsed. I hope nothing has come in the way to prevent you from prosecuting your important plan. From the nature of your subject you must not look for a very rapid sale, you will not therefore, I trust, be disappointed if the book should go slowly off. Those only who have made some progress in the science will be interested in your speculations.

I write you at present to give you some information respecting your *atomic* theory, which I hope will not come too late for your second volume. Berthollet has written a long attack upon it in the introduction to the French translation of my *System of Chemistry*, a book which I have not seen and cannot therefore give you any account of his argument. But in the second volume of the *Mem. D'Arcueil* which Mr. Chenevix brought over, and of which I have got a copy, there are several dissertations which I wish you saw. Berthollet has repeated your experiments respecting the spontaneous mixture of different gases. The apparatus nearly resembled yours, but was more elaborate. The gases were always uniformly mixed

in twenty-four hours if one of them was hydrogen (as hydrogen and carbonic acid, hydrogen and oxygen, hydrogen and azote) ; but other gases did not mix uniformly in that time (as air and carbonic acid, azote and oxygen, azote and carbonic acid, oxygen and carbonic acid). Air and carbonic acid did not mix uniformly in seventeen days. In the highest globe there were forty-two of carbonic acid, in the lowest fifty. These experiments are rather adverse to your peculiar opinion respecting the gases. Berthollet in one other dissertation denies that there is any such gas as *carbonated hydrogen*. I have never examined the gas from marshes, which I take to be the only carbonated hydrogen gas known ; but I certainly shall next summer. You have, and upon your authority I went. I trust I shall find you correct. Every gas from animal and vegetable substance, and from salt, which I have tried, and I have tried a great many, contains oxygen, so that I cannot from my own experience contradict Berthollet. Dr. Henry's experiments are similar to mine, except that his opinion about the presence of pure hydrogen gas in some of his gases appears improbable. Berthollet admits the accuracy of the experiments adduced by Dr. Wollaston and me in support of your theory. But he says it does not apply to the *sulphates*. He quotes my analyses of the sulphates of potash, and gives several of his own of a similar nature. My experiments were made with care ; but the results give negative conviction, as I went

on wrong data respecting the composition of sulphate of barytes. The most important paper respecting your atomic theory is by Gay-Lussac. It is entirely favourable to it, and it is easy to see that Gay-Lussac admits it, though respect for Berthollet induces him to speak cautiously. His paper is on the combination of gases. He finds they all unite equal bulks, or two bulks of one to one of another, and three bulks of one to one of another. The following are his facts :—

			Bulk.	Bulk.
Ammonia	.	.	is composed of 100 azote and	300 hydrogen.
Sulphuric acid	.	.	" "	100 sulphurous acid 50 oxygen.
Muriate of ammonia	"	"	" "	100 ammoniacal and 100 muriatic acid gas.
Carbonate of ammonia	"	"	" "	100 do. 100 carbonic acid.
Subcarbonate of ammonia	"	"	" "	100 do. 50 do.
Fluoborate of ammonia	"	"	" "	100 ammoniacal gas 100 fluoboric acid gas.
Subfluoborate of do.	"	"	" "	100 do. 50 do.
Water	.	.	" "	100 hydrogen 50 oxygen.
Oxide of azote	.	.	" "	100 azote 50 oxygen.
Nitrous gas	.	.	" "	100 do. 100 do.
Nitric acid	.	.	" "	100 do. 200 do.
Nitrous acid gas	.	.	" "	300 nitrous gas 100 do.
Nitric acid	.	.	" "	200 nitrous gas 100 do.
Oxymuriatic acid	.	"	" "	300 muriatic acid gas 100 do.
Carbonic acid	.	.	" "	100 carbonic oxide 50 do.
100 carbonic oxide	.	"	" "	" " " " " " 50 do.

In some of these results I had anticipated him, as may be seen in my *System*, third edition. He says your experiments on the nitrous gas eudiometer are inaccurate. Oxygen either combines with 2^{ce} its bulk of nitrous gas or with 3^{ce} its bulk. His method is to add a sufficient quantity of nitrous gas in a wide vessel, and not to agitate: $\frac{1}{4}$ of the

diminution is oxygen. These are the most important facts respecting gases contained in the volume above alluded to. I thought it right to let you know them, that you might repeat the experiments, and either constate or refute them in your next volume. I shall repeat them when I have as much leisure, which is not at present. There is a dissertation on the respiration of fishes by Humboldt. He finds that not only the oxygen gas but part of the azote also in the water disappears. The water of the river Seine was found to contain 0.075 of gas. This gas contained about 31 per cent oxygen, the remaining 69 were azote. These proportions also differ from yours. Gay-Lussac has shown in a dissertation that the quantity of acid which combines with a metallic oxide is always proportional to the quantity of oxygen which it contains. Thus if two oxides a and b contain the first one, and the second two of oxygen, b will combine with twice as much acid as a . If this rule hold it furnishes a very easy method of ascertaining the composition of metallic salts. The fluoboric acid mentioned in the preceding table is obtained by heating fluuate of lime and boracic acid. It is a compound of boracic and fluoric acids. It has been demonstrated by Davy and by Gay-Lussac and Thénard, that muriatic acid gas contains at least $\frac{1}{4}$ th of water essential to its gaseous state. Pray make my best respects to Dr. Henry. I have been looking for his dissertation on common salt in

the journals, but it has not yet made its appearance. I send you two copies of a paper of mine, printed some months ago. But the copies were somehow mislaid till the other day.—I am, dear sir, yours faithfully,

THOMAS THOMSON.

H. Davy to Dalton

My dear Sir—I should be glad if you would inform me by what process you procure phosphoretted hydrogen, weighing 25 grains the 100 cubical inches, as I should like to examine this gas.

I am surprised that you should not have read in my paper the examination of the quantity of water in potash. I rate it at 16 per cent; but this water does not exist in the potash formed by combustion from potassium. See the end of the first section.

I have no objection to the theory that the metallic oxides and earths are compounds of water and unknown bases; but then fused potash must contain two of water. With respect to whether the metals of the alkalies are compound or simple, I do not think that of any importance as to the discovery, but of great importance as to theory, and in all my papers I have taken the two views. But the French view is absurd; they assume that *potash* is a compound of water, and something which cannot be procured free from water, and yet they

call potassium a compound of *potash* (assumed to be a compound of water) and hydrogen. It certainly may be a compound of an unknown alkaline basis and hydrogen.

You ask what becomes of the water in the galvanic processes. It is decomposed, and hydrogen is always disengaged at the negative surface when the battery is in high action.

When fused potash is passed over iron turnings the water of the potash is decomposed with the alkali, and torrents of hydrogen come over, holding potassium in solution.

I shall be sorry if you introduce into your rising system an hypothesis which cannot last concerning the alkaline metals.

I will let you know when the managers can settle your account.

I am now opposing a result which I cannot get over of the conversion of ammonia into oxygen and hydrogen.—I am, my dear sir, with much esteem and regard, faithfully yours,

H. DAVY.

FRIDAY, 25th May 1810.

NOTE

The paper here mentioned is the Bakerian lecture for 1809, read 16th November 1809 and published in the *Philosophical Transactions*, 1810.

Dalton in the *New System*, part ii., published in November 1810, gives two accounts of potassium

and sodium, one (pp. 260 and 262) in the earlier portion of the book, in which they are looked upon as metals, and the second under the headings of "Potassium, or Hydruret of Potash," and "Sodium, or Hydruret of Soda," in the concluding portion (pp. 484 and 502). In this last account Dalton takes up the view which he ascribes to Gay-Lussac and Thénard, that potash is undecomposed, and potassium is a compound of this with hydrogen. Dalton describes the product of combustion of potassium in oxygen as "potash as dry as possible to be procured, according to Mr. Davy; that is, the first hydrate," containing 16 per cent of water; whereas in the letter before us Davy expressly says that the 16 per cent of water present in fused potash "does not exist in the potash formed by combustion from potassium."

Davy's account of the French view appears to differ from Dalton's, as according to the former Gay-Lussac considered potash to be a compound of water, and something which cannot be procured free from water. The difference is, however, only apparent, as it is this "something" to which Dalton assigns the name potash and the weight 42 (*New System*, p. 486).

T. C. Hope to Dalton

2nd January 1811.

Dear Sir—Accept of my best thanks for the copy of your second volume, which Mr. Holland

conveyed to me. I should have returned my thanks sooner, but I was unwilling to acknowledge its arrival till I could say I had carefully perused the work. I have done so both with much interest and advantage. You have increased our stock of chemical knowledge by many valuable facts.

I need not conceal from you that I am by no means a convert to your doctrine, and do not approve of putting the result of speculative reasoning as experiment.

Still, however, I admire the ingenuity of your speculations, and the happy adjustment of its subordinate parts.

It must be gratifying to you to see your doctrines adopted by the first names in the chemical world. With sentiments of respect.—I am, dear sir, your very obedient servant, THOS. CHAS. HOPE.

T. Thomson to Dalton

30 GILMORE PLACE, 10th August 1812.

Dear Sir—When I left London in March I intended to have returned immediately, but several unforeseen circumstances have detained me here all summer. Owing to this your letter lay long in London. I did not receive it till lately, and could not therefore write you an answer sooner.

I have been obliged to put off the commencement of my journal till the 1st of January, but have not by any means laid aside the plan. I am

much obliged to you for your paper on the oxy-muriates which you offer, and shall accept of it most thankfully. I doubt not from your great acuteness that you will throw considerable light on that difficult subject. I have a few papers on various chemical subjects of no great value I fear ; but such as they are they will increase our information, and I mean to insert them in my journal when it appears.

When I came home to-day I found your paper on "Animal Heat" on my table. I return you thanks for it, and shall read it immediately with attention. I presume that I am already acquainted with the theory which you adopt, viz. Dr. Crawford's. It appeared to me till lately a complete explanation of the subject. But I confess I have now altered my opinion. There is a paper by Dr. Currie in the *Philosophical Transactions for 1792*, giving an account of a set of experiments which he made in consequence of a shipwreck that happened at Liverpool. These experiments have not been attended to. They struck me forcibly last winter when I was engaged in writing the *History of the Royal Society*, and appear to me to be utterly inconsistent with Crawford's theory and to overturn it. Mr. Brodie's experiments you have seen. They are also rather hostile to Crawford's theory, though of themselves I do not consider them as sufficient to overturn it. They are equally inconsistent with Dr. Currie's experiments. Dr. Crawford's ex-

periment respecting the specific heat of venous and arterial blood must be repeated, and I mean to repeat it the first opportunity.

I set off in a few days for Norway on a mineralogical expedition. I mean to cross that kingdom and go to Stockholm, visiting the principal Norwegian and Swedish mines. I expect a great fund of entertainment and information. I propose to be in London in October. If you send up your paper, which I should like to get by the end of October, address it to Mr. Baldwin, bookseller, 47 Paternoster Row. Compliments to Dr. Henry.—I am, dear sir, yours faithfully, THOMAS THOMSON.

NOTE

“On Respiration and Animal Heat” (read 21st March 1806), published in *Manchester Memoirs*, ii. S.S., p. 15 (1813).

Crawford’s theory was that in the lungs the blood gave out carbonaceous matter which combined with oxygen to form carbonic acid, and the heat thus liberated was taken up by the blood which had by the process become arterial and of greater specific heat. During the circulation this heat was given out in order to supply the waste from the body and the process repeated.

Currie’s experiments (*Philosophical Transactions*, 1792, p. 199) were on the effect of immersion in cold water on the human body, and he found that this

treatment occasioned a sudden fall of temperature followed by a gradual rise. This rise was not accompanied by any acceleration of the circulation, as would be required by Crawford's theory.

Berzelius to Dalton

LONDRES, ce 1 Août 1812,
LEICESTER SQUARE 27.

Monsieur !—Vous m'avez beaucoup obligé par le présent de votre ouvrage sur le *nouveau Système de la Philosophie Chimique* ; lequel me fit d'autant plus de plaisir, que j'avois longtemps souhaité de connoître vos idées sur un point chimique qui m'avoit longtemps occupé.

Malheureusement je ne l'ai reçu que peu de jours avant mon départ de Stockholm, ainsi je n'ai pas encore eu tems que de le *parcourir* ; et je trouve qu'il mérite d'être étudié. Il y a plusieurs points où nos résultats ne sont point parfaitement d'accord, j'aurois souhaité que le temps que je puis dépenser sur mon voyage m'auroit permis d'aller vous voir à Manchester, afin que nous aurions pu discuter cette matière de vive voix ; mais malheureusement pour moi je suis obligé à renoncer à cette espérance. Je resterai à Londres jusqu'au commencement du mois d'octobre ; je le considérerais comme un grand bonheur pour moi si vos affaires vous y amèneront pendant ce tems-là !

Agréez, Monsieur, les sentiments de la plus

parfaite considération pour vos talents distingués avec lesquels j'ai l'honneur d'être, Monsieur, votre très humble et très obéissant serviteur,

JAC. BERZELIUS.

P.S.—Je prends la liberté de vous envoyer ci inclus une dissertation de M. Gilbert sur les proportions déterminées. Cette dissertation est le commencement d'un ouvrage plus détaillé qu'il s'est proposé de publier.

Dalton to Berzelius

MANCHESTER, 20th September 1812.

Respected Friend—I see your letter of the 1st ult., and the acceptable present which you were so good as to transmit along with it. I have been gratified with perusing it; but much more with the perusal of your own papers in the *Annales de Chimie*, a regular series of which I have lately received up to March 1812 inclusive.

I have been induced to compare your results with my own, and am glad to find that in general there is as near an approximation as we have a right to expect in the present state of the science. We are agreed that an ultimate portion of sulphur, for instance, is nearly twice the weight of one of oxygen, as exhibited in sulphuric acid and oxide of lead. My numbers for the atoms of sulphur and oxygen are 13 and 7 respectively; but on further

consideration I am inclined to adopt 14 as the nearest integer for sulphur; and I am disposed to modify certain other numbers which I have enclosed in parentheses below. Your numbers and mine will then be compared as under:—

	Berzelius.	Dalton.
Oxygen . . .	7	7
Sulphur . . .	14	14
Lead . . .	90	95 (90)
Carbonic acid . . .	19 +	19.4
Barytes . . .	67 or 68	68
Copper . . .	55 or 56	56
Silver . . .	88.6	100 (90 or 92)
Muriatic acid . . .	23	22 (23)
Iron . . .	48	50
Potash . . .	41	42
Soda . . .	27	28
Ammonia . . .	14	12
Lime . . .	25	24 (25)
Zinc . . .	57	56
Phosphoric acid . . .	25 or 26	23 (24), etc. etc.

You adopt the ratio of oxygen to hydrogen in water as well as Davy, $7\frac{1}{2}$ to 1 upon the single authority of Biot; I am inclined to prefer the ratio of 7 to 1, which has so many authorities in its favour.

There are at least 5 sulphurets of iron.

I. S.

1. $50 + 14 = 78 + 22$. Vauquelin, *An. de Chimie*, lately.
2. $50 + 28 = 64 + 36$. Hatchett, *Philosophical Transactions* on magnetical pyrites.
3. $50 + 42 = 54\frac{1}{2} + 45\frac{1}{2}$. Hatchett and Proust.
4. $50 + 56 = 47 + 53$. Hatchett.
5. $50 + 168 = 23 + 77$. Got by sulphate of iron and sulphure of lime.

The red oxide of lead, I apprehend with Proust, is the *yellow and brown* oxide combined. The black oxide of iron is the second, and the red the third, the first not being yet ascertained.

Your analysis of the *yellow powder* from sulphate of iron I imagine is not quite correct. The powder is 1 atom of oxide + 1 of acid ; the oxide is 64 or rather perhaps 71 + 35 sulph. acid : by heat the acid is driven off and leaves about from 60 to 71 red oxide.

My ideas accord with yours on oxymuriatic acid and muriatic acid. Potassium and sodium I now consider as metals ; calcium, barium, etc., as somewhat doubtful.

I cannot at all enter into your disquisitions and Davy's on what you call *ammonium*. I consider azote and hydrogen as simple substances, as far as is yet known.

The French doctrine of *equal measures* of gases combining, etc., is what I do not admit, understanding it in a mathematical sense. At the same time I acknowledge there is something wonderful in the frequency of the approximation.

The doctrine of definite proportions appears to me *mysterious* unless we adopt the atomic hypothesis. It appears like the *mystical ratios* of Kepler, which Newton so happily elucidated. The prosecution of the investigation can terminate, I conceive, in nothing but in the system which I adopt of particle applied to particle, as exhibited in my diagrams.

I have no expectation of visiting London shortly, and should have been glad if your views had led you to visit this place, and to *time* an opportunity of chemical discussions on those points where we may differ. I should have wrote sooner, but I wished to read your papers first that I might throw out a few observations.—I remain with great esteem,
yours truly, JOHN DALTON.

NO. 10 GEORGE STREET.

P.S.—If you do not favour us with a visit here, I shall be glad to hear from you again before you leave this country.

Berzelius to Dalton

LONDON, *ce 16th October 1812.*

Monsieur !—Bien de remerciements pour votre obligeante lettre, à qui j'aurois dû avoir répondu il y a longtemps, si non des petits voyages aux environs de Londres m'auroient empressé de rien entreprendre. Je suis à présent au point de m'en aller, et j'ai crû devoir vous prier de m'honorer de vos communications même quand je serai de retour dans ma patrie, je ne manquerai point à vous faire part de tout ce que (je) puis avoir d'intéressant à vous mander.

L'observation que vous venez de faire sur le sous-sulphate d'oxide de fer est parfaitement fondée, aussi je m'appercevois de l'inexactitude de cette

analyse lorsque je trouvai la loi d'après laquelle l'acide sulphurique se combine aux bases salines. Vous trouverez une discussion détaillée sur cette matière dans les *Annales de Chimie*, dans la partie de mon dernier traité où j'ai parlé des sels à eaux de base. Dans le vrai sous-sulphate l'acide est combiné avec 6 fois autant d'oxide de fer que dans le sulphate neutre. Vous verrez aussi à cet endroit quelle substance singulière que fut la poudre jaune, que j'ai pris pour sous-sulphate pur dans mon premier traité. Vous appelez le sulphate d'oxide de fer ordinaire un supersulphate ; je ne puis pas en voir la cause, parceque l'acide y neutralise une quantité de base dont l'oxigène est $\frac{1}{3}$ de celui de l'acide, tout comme dans le sulphate neutre de potasse.

Votre opinion que le minium est une combinaison de l'oxide noir avec l'oxide jaune, est peut-être fondée sur la difficulté de concevoir un demi-atome ; je crois qu'il faut laisser les expériences mûrir la théorie. Si celle-ci commence à s'occuper de presser la nature dans les formes, elle cessera d'être utile et de se perfectionner. Vous avez raison en ce que la théorie des proportions multiples est un mystère sans l'hypothèse atomistique, et autant que j'ai pu m'apercevoir tous les résultats gagnés jusqu'ici contribuent à justifier cette hypothèse. Je crois cependant qu'il y a des parties dans cette théorie, telle que la science vous la doit à présent, qui demandent à être un

peu altérées. Cette partie p. ex. qui vous nécessite de déclarer les expériences de Gay-Lussac sur les volumes des gases qui se combinent, pour inexactes. J'aurois cru plutôt que ces expériences étoient la plus belle preuve de la probabilité de la théorie atomistique, et je vous avoue d'ailleurs que je ne croirai pas si aisément Gay-Lussac en défaut, surtout dans une matière où il ne s'agit que de mesurer bien ou mal.

Mais le papier m'ordonne à finir. Si vous vouliez m'honorer de vos lettres, mon adresse sera ci-après *Stockholm*, sans autre adresse plus particulier ; je pars demain au soir pour me rendre par Marverg à Gottembourg. — Que Dieu vous bénisse.

J. BERZELIUS.

NOTE

In the very interesting comparison of results contained in Dalton's letter to Berzelius, Dalton's numbers are (for the most part) those published in the *New System*, part ii. (1810). The numbers ascribed to Berzelius have been calculated from those actually given by the Swedish chemist, which were all referred to $O = 100$. In many cases it has been necessary to divide by 2 to obtain comparable numbers.

A translation of the second of the letters from Berzelius has been published in Henry's *Life of Dalton*. It is added here in the original for the sake of completeness. A number of accents have

been added, but the construction has not been altered.

Berzelius' first analysis of the "yellow powder" (Gilb. *Ann.* 37, 308), gave the result—

Sulphuric acid	.	.	.	27.33	100
Ferric oxide	.	.	.	72.67	266
				<u>100.00</u>	<u>366</u>

According to which the acid neutralises 4 times as much base as in the neutral sulphate—

Sulphuric Acid	.	.	39.56		65.5
Ferric Oxide	.	.	60.44		100

According to Dalton, on the other hand, the powder contained one atom of oxide to one of acid, and therefore had the composition—

Acid	.	.	.	35	33	100
Oxide	.	.	.	71	67	203
				<u>106</u>	<u>100</u>	<u>303</u>

As explained by Berzelius in the following letter, referring to the paper published in Gilbert, 40 (1812), 294, the true subsulphate of iron was found to contain—

Acid	.	.	.	20.2		100
Oxide	.	.	.	79.8		395

The specimen analysed was prepared by saturating sulphuric acid with ferric oxide, partially precipitating with ammonia, and digesting the brownish-red precipitate with the liquid. The "yellow

powder," originally obtained as a deposit from a solution of ferrous sulphate, and of the composition stated above, was then again examined. A sample procured from a vitriol works had the composition—

Acid	. . .	15.9	100
Oxide	. . .	62.4	392.52
Water	. . .	21.7	

and therefore contained acid and oxide in the same ratio as the brownish-red precipitate just described. Another sample was prepared in the same way as the first one, viz. by dissolving iron in dilute sulphuric acid, to which a little nitric acid had been added, and then exposing the solution to the air for some days at $25-30^{\circ}$ in contact with slips of metallic iron.

The yellow precipitate was found to contain—

18.5	of water strongly charged with ammonia.
32	„ acid.
49	„ oxide.

And was therefore an ammoniacal compound.

The “disquisitions on ammonium” (Gilbert, 40 (1812), 176 *et seq.*), consist of an elaborate exposition of the result of assuming that ammonia contains oxygen.

The analogy of ammonia with the alkalis, its basic properties, and the production of ammonium amalgam, led many, and among them Berzelius, to think it possible that ammonia really contained oxygen, the discovery of which in potash and soda

was the recent and brilliant achievement of Davy. Now ammonia is decomposed by electricity into nitrogen and hydrogen, in which, therefore, the oxygen must be contained. According to the dualistic theory the nitrogen and hydrogen would then both be oxides, the combination of which to form ammonia would be quite analogous with that of oxide of sulphur and oxide of potassium to form sulphate of potash.

According to Berzelius nitrogen and hydrogen would, under these circumstances, have to be considered as oxides of an unknown substance—*ammonium*—their composition being—

		H.	N.
Ammonium	. . .	90.062	43.027
Oxygen	. . .	9.938	56.973

When the elementary nature of nitrogen and hydrogen had been finally established, the term ammonium was transferred to the group of atoms contained in the salts formed by the union of ammonia with acids, in which sense we still employ it.

Dalton's views on the combination of gases by volume have already been discussed (p. 47).

J. Otley to Dalton

Mr. Dalton—Sir—I received yours of the 8th, and am much obliged to you for the analysis of

the gas. The books for Mr. Knight shall be carefully forwarded.

Derwent Lake varied very little in height for a month after you saw it, which was unusually low for such a length of time. About the 6th of August the floating island began to appear above water; I was upon it on the 21st, at which time the lake had risen about 8 inches, and the island was only in its highest parts about 4 inches above water; its length was 88 yards, its greatest breadth 25; but some parts of it was less than half that breadth. The gas on coming up (by boring under water near the edge of the island) had then a very perceptible smell, which I compare to that of a foul gun. Whether this smell is strongest when the island first emerges, or whether at other times it is taken away or lessened by the greater depth of water through which the gas ascends I am not able to determine.

I endeavoured to ascertain whether the island consisted of the same kind of peat earth throughout, which I find to be nearly the case; and also to examine more particularly the earth underneath it, which I have been inclined to call a vegetable oxide. On taking up some of this at the depth of 13 feet below the surface, I found it intermixed with specks of a bluish-green colour, which from its turning black with infusion of galls I take to be a sulphate of iron. This makes me suspect that in my hypothesis of the generation of the gas I may

have laid too much stress upon the decomposition of the vegetable matter of the island ; or could the iron be originally contained therein ?

The gentleman who brought your letter having kindly proffered to take anything I might wish to send, I embrace the opportunity of sending you a small specimen of the earth of the island, taken at 1 foot below the surface ; a smaller one from the under surface of the island, and another, that with the clayey appearance, from beneath the island at the depth of 13 feet below the surface, that is 4 feet below the water under the island. This you will find when dry to be uncommonly light. From knowing the qualities of these substances you will be able to form an opinion where it is most likely for the gas to be generated.

The island never appeared so high above water this season as it did in 1808, and on the 1st of September, the lake having risen about 2 feet, it was entirely covered, and so it remains. At present, though, the lake is now considerably fallen.

A writer in the *Cumberland Pacquet* has advanced an opinion of the island being raised by the air contained in the leaves of the plants growing upon it, viz. the *Lobelia Dortmanni* and *Isoetes Lacustris*. This, I think, requires very little consideration to refute it.—I remain, sir, your very humble servant,

JONA. OTLEY.

KESWICK, 14th September 1815.

P.S.—The earth taken from beneath the island I find useful in cleaning the cases of watches.—
J. O.

L. Howard to Dalton

TOTTENHAM, 12th mo. 13, 1816.

Esteemed Friend—I shall willingly give thee some account of our process for making sulphuret of potash. Our method is to mix dry subcarbonate of potash with sublimed sulphur and throw them into a crucible heated to redness, effecting the fusion as quickly as possible: there is an effervescence at the moment of the union, indicating that the sulphur expels the carbonic acid. As the sulphur burns freely the whole time, some of it must be lost, but our last account of the proportions stands thus :—

135 lbs. kali prop.
27 lbs. flor. sulph.

Pro. 108 lbs. kali sulph.

So that the loss in carbonic acid, water, some portion burned and volatilised, and a little waste, is 54 lbs.

The colour of the product varies in different parts from straw to liver colour. Is this from a different proportion of sulphur retained, or its different degree of oxidation? The Pharmacopœia, I think, orders half the weight of the alkali in sulphur. *We* use one-fifth, all above which I should

consider as wasted, but I have never examined the proportions in which potash and sulphur really exist in our compound, which in appearance is like that of other chemists.

If a set of my meteorological observations as published in Nicholson and Thomson will be acceptable, I will send them on thy indicating by what conveyance. I know not whether the present will be in time for Thomas Hoyle. I should be glad to receive from thee any striking facts in *this* line, as I have some thoughts of endeavouring to bring the mass of materials, which I have been now for ten years collecting, to bear upon the subject in the form of a few familiar lectures. I think thou once gave me an account of a remarkable electrical appearance on the *cross* of your parish place of worship, which, if it was not *during* an actual thunderstorm, would be valuable to me, if stated with the time, place, and circumstances. I have rummaged the *Philosophical Transactions* and divers other works for the most appropriate instances of various metereological phenomena, and shall be in some respects much indebted to thy own and other papers in the *Manchester Memoirs*. Pray what is the most recent publication of these; or is there anything since vol. v. p. 2? My barometer has lately indicated the highest and lowest points for the last twelve months, viz. 30.63 inches on the 30th ult., being the middle of a week's elevation, and 28.60 inches last night, the

12th being the crisis of a very short depression, preceded by quick oscillations for a week past. We had a storm of wind the forepart of the night, and thunder and hail to-day at noon. Our rain for the year is on the point of exceeding 30 inches, a very large amount for this part of the island, and we may yet have an inch or two more. I met with little weather but thunderstorms and wet in our late tour on the Continent, which, however, did not deprive me of a most sublime and inconceivably extensive view of the chain of the Alps as we approached from the south of Germany, being at the time on some very high calcareous ground near Duttlingen, and not far from the sources of the Danube, but at full 150 miles from the background of our prospect, which, being seen wholly through the upper and clear atmosphere, we could distinguish the light and shade of every mountain, and determine what was rock, what turf, what snow, and what glacier, with as much ease as I have usually been able to distinguish here at one tenth of the distance. I noticed on my first getting back the difference between the Continental atmosphere and our own in point of transparency, even in so wet a summer, was quite striking; as was likewise the smallness of the features of the landscape in our little island compared with the bolder sweeps of the Continent.

I shall be glad to hear from thee at thy leisure, and remain thy sincere friend,
LUKE HOWARD.

T. Thomson to Dalton

GLASGOW, 13th August 1818.

My dear Sir—I regretted very much not having the pleasure of meeting you when I was in Manchester about a month ago. But my time was so limited that I could not spare three days which a journey to Keswick would have taken up. I have been under the necessity of resuming the sole editorship of the *Annals of Philosophy*, very much against my inclination. Several very awkward things took place in consequence of my having my name standing as editor to a journal over which I had no control. I wished of course to have my name struck off the title-page. To this the bookseller objected with so much obstinacy that I was obliged to resume the sole editorship as the only alternative. Unluckily I was totally unprepared for this step, and am quite destitute of materials. I must therefore solicit the assistance of my friends to help me out for a number or two by their contributions. Upon you in particular I reckon with some confidence, and will take it as a particular favour if you would favour me with a paper by the 1st of October, for I shall have the November number to edit. The subject, of course, I leave to yourself. No subject of experiment from you can come wrong. I was happy to learn from Dr. Henry that you had begun to print.

You will find the investigation of the metallic oxides particularly difficult. Our present methods are bad, because we cannot distinguish between mixtures and chemical combinations. Many of Berzelius' determinations are certainly wrong, particularly the oxides of antimony. I suspect that some of the vegetable acids unite not to the oxides but to the metals themselves, at least in some cases. Thus I think that oxalate of zinc is a compound of oxalic acid and zinc. But these observations are *entre nous*, to be ascertained hereafter. The gases constitute the department of chemistry capable of the most accurate investigation. You will find the doctrine of volumes (as soon as you are satisfied of its accuracy) peculiarly valuable as a method of investigation. I am just beginning to fit up my laboratory.—I am, dear sir, yours faithfully,

THOMAS THOMSON.

P. Harris to Dalton

EAGLESFIELD, 12th mo. 19th, 1821.

My much esteemed friend John Dalton—I sat down at my desk yesterday afternoon at half-past one to reply to thy last favour a few weeks ago, but before I got pen to paper it came on so particularly dark I could not see to write (and thou knows my desk is not above five feet from the window). I soon found the cause with a clear witness. Almost immediately commenced nearly one of the

most awful thunderstorms I ever remember. I am now this day fifty years and eleven days old, and I or none in this past that I have yet conversed with ever remember such a one this time a year, and it is a matter of doubt whether there has been any like it even in summer. Distant thunder was heard all the morning and forenoon, but nothing particular to make any remark of, but this sheet whereon I am now writing, a little after half-past one, was covered with a reddish part tinged with blue flash of lightning for a moment, and immediately after, I think I almost may say safely, one of the loudest peals of thunder I ever heard; it made my house to shake, doors and windows, etc., and continued in this way for nearly half an hour—thunder and lightning succeeding each other alternately, with torrents of rain and hail. At same time I sat pensive and quiet considering the awfulness of the scene. On looking towards the fire I perceived the irons with pretty sharp tops towards the chimney, and knowing sharp points of iron attract the lightning from Benjamin Franklin's experience, I thought I would lay them horizontal on the fender. Before I had done that, on taking my hand off them, it and the irons were totally covered with lightning for a moment, but no injury to me.

I do not as yet hear of any lives being lost, but at Dean Scales, about a mile off us, the lightning entered a chimney or roof and nearly destroyed

two beds, tore up the floor, etc., and at Blind Crake something similar. A person just left me says he sheltered under a tree near it which the lightning struck, but he escaped without much injury. It came in a southern direction, I am informed, from the mountains—the Pillar, Knockmurton, etc. etc.

I feel greatly obliged to thee for thy attention respecting the dial. On considering thy remarks respecting it I think it may be the best for me to get a round stone properly done a little below the plate, towards the ground, with O. G., etc., agreeable to some of the orders of architecture, and about $11\frac{1}{2}$ or 12 inches over at top, not quite finished, but so as the mason can do it when put up or before. (We have a very good one here.) I should feel much gratifyd if thou could make it convenient to do it when down in 7th month next, when we hope to have the pleasure of seeing thee here. I think if three pieces of brass about $\frac{1}{2}$ or $\frac{3}{4}$ of an inch long could be soldered or screwed on the underside of it about an inch from the margin, a little thicker at the bottom, and about $\frac{1}{2}$ an inch diameter, they might be let into the stone by pouring melted lead into the hole, and immediately putting the dial plate on before the lead stiffened, or make a small cutting in your stone under your plate to your lower side to pour your lead in after and make it fast. I had no intention when I mentioned your dial to thee but to put it up at Pardshaw

Hall, but on considering I propose to have it in my own garden here. I may get one after for there, but, however, as the initials Dr. D. is put on let them remain. They may be seen at Eaglesfield many years after thee and I've gone.

With respect to sending it, William and Jonathan Harris has occasionally cotton twist coming from Tatlock and Love, Manchester. Perhaps it might be enclosed safe in one of these parcels in a wood box. If thou thinks that mode of conveyance safe I will direct W. and J. to inform their friends to call on thee, or perhaps thou could on them, and if thou has time thou can see if that mode will not hurt the gnomon when packed, it being the most particular part to attend to. I have been rather unwell for two or three weeks in something like a rheumattick complaint, pain in my back, etc. I am a little better at present, though not able to stir much out of doors, yet the weather has been remarkably stormy here for a few weeks. Strong winds, and of course much damage in shipping, as also at Liverpool, etc. etc. It might be expected after such a dry summer. Thou would hear of the rather sudden and unexpected removal of our worthy friend Wilkinson.

My brother Wm. Harris is a little confined in a cold at present. My dear S. H. is pretty well, and desires to be kindly remembered to thee.—I am respectfully thy friend,

PONSONBY HARRIS.

N.B.—Could ye year 1822 be engraven on any part without hurting the line or figure, etc. If it could I should like it to be done.

L. Howard to Dalton

LONDON, 5th mo. 31, 1822.

Dear friend John Dalton—I have to request thy acceptance of the copy marked for thee of the within paper, and likewise the favour of getting delivered for me the two other copies to their respective addresses. The Royal Society has nominated a committee for examining into the state of the meteorological institute belonging to it, which, having existed several months, has, I believe, done nothing as yet. The only time I have attended it we were chiefly occupied about the best mode in theory of ascertaining the exact height of the column in the barometer, and could by no means agree upon it. Dr. Young seemed exceedingly difficult to satisfy on this point. For my own part I think it of much more consequence to meteorology that observations be constantly and faithfully, than that they be very minutely, made. We must creep before we fly in this infant science. The astronomers have got the start of us by some thousand years, and *they* may boast of their subdivisions of seconds, and be as rigorous as they please, and predict with just confidence, while *we* can with difficulty make out a theory for any train

of phenomena, and are forced to grope on in conjectures. Howsoever, if the science continue to obtain the attentions of really capable men, we shall see something perhaps before *we* die that is worth notice in it. Wouldst thou have supposed that we have yet a bishop among our labourers. Such is the fact. The good old Bishop of Durham sent for me some time back to put into my hands about fifty years' observations on the barometer and thermometer, with remarks on weather, etc., kept by himself (when at home, and in his absence by his gardener) at his seat in Oxfordshire. I made up the year 1821 and sent him results, which agreed very well with ours near London, and I think the set, continued so long and with but little interruption, likely to be valuable to future investigators. My kind regards to Dr. Henry when thou seest him. A letter from thee is always acceptable to thy affectionate friend,

LUKE HOWARD.

T. Thomson to Dalton

GLASGOW, 14th April 1823.

Dear Sir — I take the opportunity of Mr. Davies's passing through Glasgow to acknowledge the receipt of your letter of October last, which Mr. Davies did me the favour to bring. It would have given me great pleasure to have forwarded Mr. Davies's view by every means in my power,

but his stay here was too short to enable him to attempt any chemical investigations.

My atomic labours are now drawing to a close. I have now determined all the simple bodies except about five or six, which are so scarce that I am afraid I can hardly investigate their atoms successfully. I have made out gold, platinum, rhodium, iridium, and am at present occupied with palladium. I have also made out a great many of the crystallised salts, and mean to prosecute the examination somewhat further. The triple salts are very numerous, and in general they crystallise admirably. I think I could almost double the list of salts.

I am at present endeavouring to deduce by simple and decisive experiments the ratio between the weights of oxygen and hydrogen gases, and oxygen and azotic gases. What I have done leads me to think that I shall be successful. My winter course is now drawing towards a conclusion, when I shall have more leisure for experimenting. Be so good as make my best respects to Dr. Henry. I meant to have written him, but am unluckily interrupted.—I am, dear sir, yours truly,

THOMAS THOMSON.

GLASGOW, 19th April 1825.

Dear Sir—I do not know whether you have lost sight of the atomic theory, but the work which accompanies this letter, and which I have

just published,¹ will show you that it has occupied a great deal of my attention ever since I came to reside in Glasgow. This work contains the sum total of my experimental investigations during my residence in Glasgow. If you take the trouble to look it over you will be convinced that I have not been idle. My experiments have amounted to many thousands, and they have been all made with as much accuracy as the present state of our means enabled me to attain. The results I think beautiful. You will see that chemistry is now raised to the rank of a mathematical science, and that, assisted by the tables which I have given at the end of the second volume, analyses may henceforth be made with much greater accuracy than heretofore.

I hope to have the pleasure of meeting you in Manchester about the beginning of June, as I mean to go to London about that time, and shall take Manchester in my way. I shall then perhaps hear how you are occupied, and whether you have anything at present on the anvil.—I am, dear sir,
yours truly,

THOMAS THOMSON.

Davy to Dalton

SOMERSET HOUSE, 10th January 1826.

My dear Sir—I have been absent in Wales during three weeks, but I never received the

¹ The work mentioned is entitled *An Attempt to Establish the First Principles of Chemistry by Experiment* (1825).

note to which you allude in your last letter, though I may have mistaken you and confounded it with one that came into my hands before my departure.

I am very happy to find that you have done the Royal Society the honour to communicate with them. I shall present your paper with great pleasure, and I hope it will not be the last that you will favour us with.

I shall feel infinite pleasure in knowing that the services you have rendered science were fully appreciated and properly rewarded; but I am afraid that in these times philosophical merit has little chance of receiving its proper meed either from the State or the public, and must trust too much to posterity.

You have, however, a sure reward in the conviction that you have not only raised an imperishable reputation for yourself, but exalted the glory of your country by your development of the theory of definite proportions.—I am, my dear sir, your sincere friend,

H. DAVY.

NOTE

Dalton's first communication to the Royal Society was entitled "On the Constitution of the Atmosphere" (1826), and was followed by two others which appeared in the *Philosophical Transactions*—"On the Height of the Aurora Borealis"

(1828), and “Sequel to an Essay on the Constitution of the Atmosphere; with some account of the Sulphurets of Lime” (1837).

D. Gilbert to Dalton

EASTBOURNE, SUSSEX, 6th August 1826.

Dear Sir—I flatter myself that you will have the goodness to excuse me for troubling you on a subject intimately connected with some of your most successful pursuits, and in which I have continued for many years to take a most lively interest.

Bred amidst the mines of Cornwall, surrounded by steam-engines, and having some on my own land, my attention has been directed from my earliest years (when Mr. Watt’s improvement was first introduced) to the theory of their construction and of the principles on which they act.

On my going to Oxford in 1785, I first acquired a knowledge of Dr. Black’s most important discovery of latent heat, when it immediately occurred to me that if several hundred degrees of heat were rendered latent in the conversion of water into steam, and if about 40° doubled its power, that an immense advantage must be derived from the use of steam carried to a power so high as the strength of materials would allow.

But in this supposition I entirely overlooked a most important element in the calculation. I

tacitly assumed that steam raised to 212° was subsequently carried up to 252° , etc., etc., without receiving fresh supplies from the generating water. But this cannot (probably) be effected on account of the non-conducting nature of steam; and consequently, as the water increases in temperature, fresh quantities, carrying with them latent heat, are sent to the former steam.

Consequently, the intensity of steam, arising from heated water at different temperatures in close vessels, becomes an element almost of equal importance with the corresponding elasticity.

For instance, if the heat rendered latent by passing from water into steam is represented by 960° , and if the capacity of steam for heat is to that of water (weight for weight) as 1.55 to 1, and if 40° double the elasticity, then taking unity for the density of the steam at 212° and d for its density at 252° , the latent heat in the latter case will be $d \times 960$. The heat absorbed to raise the temperature is $d \times 40 \times 1.55 = d \times 62$. Suppose them $= 2 \times 960$, in which case there will neither be gain nor loss, then $d \times 1022 = 1920$, or $d = \frac{1920}{1022} = 1.88$.

I presume that the density is not so great as the above, but that it is very considerable appears from the small advantage gained by the use of strong steam in relation to the fire consumed.

Now if you have any direct experiments or deductions, which coming from you I should

esteem almost as authentic as experiments themselves, you would confer a great obligation on me by communicating them.

I have so many occupations in London, during the sitting of Parliament, that it is scarcely in my power to consult public libraries, and having last year ordered the whole of those most valuable works, by which you have instructed the scientific world, I was extremely disappointed by an answer informing me that they were out of print.

I can rely on your well-known zeal in everything connected with the progress of investigation and discovery for excusing my freedom in thus addressing you, and I remain, dear sir, your very faithful and humble servant,

DAVIES GILBERT, F.R.S.

T. Thomson to Dalton

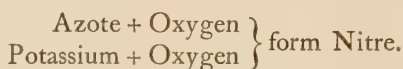
GLASGOW, 8th December 1826.

Dear Sir—This letter will be delivered by Dr. Colquhoun, an old assistant of mine, who has gone up to Manchester on business, and is anxious to be introduced to you. He is a very well-informed man and an excellent chemist, and would be very likely, unless he be absorbed (as has hitherto been the case with all my promising pupils here) in the vortex of manufacture and business, which is here all powerful. He has

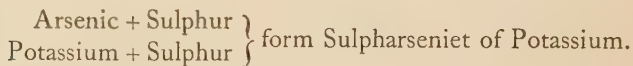
already written several good papers, which have appeared in the *Annals of Philosophy*.

I am at present occupied chiefly with mineralogy, I mean to analyse every mineral not hitherto accurately analysed as far as I can get specimens of them.

A very curious paper has been just published by Berzelius. There are four bodies, oxygen, sulphur, selenium, and tellurium capable of forming salts by combining with acid and alkaline bases. Oxygen in this way forms all the salts hitherto known. Thus



Sulphur may be substituted for oxygen and constitute a new set of salts as numerous as those hitherto known. Thus



Selenium may be substituted in the same way for oxygen and sulphur, and so may tellurium.—I am, dear sir, yours truly, THOMAS THOMSON.

Pray make my best respects to Dr. Henry when you see him. I saw his son some time ago on his way to Edinburgh.

D. Gilbert to Dalton

EASTBOURNE, SUSSEX, 15th January 1828.

Dear Sir—I have this morning been favoured with your letter of the 11th; and I answer it at once, to say that I am sure the Royal Society will be most happy to receive any communication with which you may have the goodness to favour them. And certainly the aurora borealis is one of those curious phenomena that demands the attention of every one, connected as it is with the height of the atmosphere and with electricity, which is itself intimately related to magnetism.

The monthly statements of work done by the steam-engines of Cornwall are certainly deduced from calculations founded on the dimensions of the boxes, plungers, and working pieces, the length of the stroke, and the length of the lift. And when boxes or plungers move in brass working pieces from 12 to 18 inches in diameter, making strokes of 8 or 10 feet, perhaps eight or ten times in a minute, I do not believe that the water escaping bears any material proportion to what is actually raised: at all events their monthly statements give an exceptionally uniform result, and in that way it appears that about two-thirds of all the loss has been saved by the recent improvements, and this is confirmed by the Custom-house returns.

I am much gratified by your approval of my last paper in the *Philosophical Transactions*. In

respect to the particular point I must confess myself to be fully convinced of the perfect accuracy of the abstract assumption, whatever may be the result of experiments. In the same way as a resistance proportionate to the squares of velocity is absolutely true, although it can only be approximated to in any physical fluid.

In the return for last November one of the engines performs 67 millions, and a trial has since been made in the presence of several captains of mines deputed for the purpose of witnessing it, when the figures exceeded 64 millions.

According to another mode of estimating, 67 millions performed by a bushel of coal weighing 81 pounds equals that weight (lifted) through an ascent of rather more than 151 miles.

I shall go to London to-morrow.

If your communication be addressed to me under cover weighing less than an ounce and not more than this, by the same post, I shall be most happy to receive them.—Believe me, dear sir, your much obliged and very humble servant,

DAVIES GILBERT.

D. Brewster to Dalton

ALLERLY BY MELROSE, 16th March 1831.

Dear Sir—Being at present engaged in some experiments on the structure of the spectrum, and on the absorption of light, I am exceedingly

anxious to learn if any change has taken place in your eyes in their insensibility to red light. You would oblige me greatly if you could give me an account of the appearance to your eye of a spectrum formed by the light of the sky by looking through a prism at a narrow longitudinal aperture formed by the edges of window-shutters nearly closed. You will understand the object I have in view when I mention that I have found the spectrum to consist of three spectra of the same length, viz. a *red*, a *yellow*, and a *blue* spectrum, so that all these three colours exist at every part of the common spectrum. Now as your eye is insensible to *red* light, but sensible to *yellow* or *blue*, the red space should not vanish, but should appear yellowish with a slight tinge of blue, the yellow being very faint.

I should like also to know if white objects appear to you yellowish with a tinge of blue, or rather green, as they should do if the eye is insensible to red light. Of course you cannot recognise the red light which exists in *violet*.

I intend to reprint in the next number of my journal your paper on this subject in the *Manchester Transactions*.

It is proposed to have a great meeting of scientific individuals in Great Britain, to be held at York on the 18th–25th July. It would be very gratifying if you and Dr. Henry could attend.—I am, dear sir, ever most faithfully yours,

D. BREWSTER.

W. Whewell to Dalton

CAMBRIDGE, 10th September 1831.

My dear Sir—I send you the copies of our transactions excepting the first part, which you mentioned that you have already, and I beg you to present them to the Philosophical and Literary Society of Manchester from the Philosophical Society of Cambridge.

I take the liberty of enclosing a packet for Dr. Traill, which I hope it will not be inconvenient to you to send to Liverpool by some of the usual conveyances.

I have made some enquiry concerning Miss Hague, whom I mentioned to you as having a similar affection of vision to your own. I have not yet heard the particulars of her case. But Professor Cumming tells me that Dr. Wollaston described to him the case of a *lady* who could not distinguish a ruby from an emerald except by the figure, and who thought a fawn colour very like a light green.

I beg my regards to Dr. Henry and the other kind friends whom I had the pleasure of becoming acquainted with in Manchester, and am, dear sir, yours very faithfully,

W. WHEWELL.

T. Thomson to Dalton

PRIMROSE, 10th May 1834.

Dear Sir—I hope you will excuse the liberty I take in forwarding to you my observations on Mr. Graham's Law of the Diffusion of Gases. I was much gratified to learn from Dr. Henry that you consider the view I have taken of the subject as sound and free from objection. My object in publishing these observations was entirely a desire that Mr. Graham's facts, which afford so striking a confirmation of your admirable theory of the constitution of mixed gases, should not be generally so misconstrued as they have been by Mr. Graham, who considers them as involving some newly discovered property of gases, and inexplicable by any existing theory.—I remain, dear sir, with much respect, yours truly,

THOMAS THOMSON.

NOTE

This letter is from T. Thomson of Primrose, the calico-printer, and not from T. Thomson, the professor of chemistry at Glasgow.

J. Dalton to H. Dalton

KENDAL, 14th December 1834.

Respected friend Henry Dalton—It falls to my lot to have the melancholy task of informing

thee of the decease of my brother Jonathan Dalton ; he died on the morning of the 11th inst. after an increased severity of his affliction for a few days ; I believe all the alleviations that could be availing were afforded : I received the account on the evening of the 11th, and arrived here on the 12th. The funeral is fixed for to-morrow morning.

I find by his will he has left all his real and personal estate to me, and made me the sole executor ; the real estate thou art acquainted with ; the personal is very small, and the debts are considerable, amounting to nearly £900 ; but about one half of this was owing to me.

I find thy letter of the 9th July 1834 with a note that it was answered by him on the 12th. I understand that my brother wrote thee (or rather got an amanuensis to write) about three or four weeks since, and no answer having come to hand yet, I judged it expedient to inform thee of the present circumstances without delay.

As I have no doubt thy agency has been satisfactory to my brother, I hope it will be continued to me : when the late half year's rent is received and disbursements paid I think it will be best to remit to W. D. Crewdson and Son, bankers here, to be placed to my account with them, and to request from them an acknowledgement of the receipt, and they may inform me as may be convenient.

Should anything occur to require my attention,

my address will be at 40 George Street or 27 Falkner Street, but "Dr. Dalton, Manchester," will generally find me.

At my distance from Eaglesfield I cannot often visit it ; but no one knows what may happen.

During my stay of two or three weeks in London last spring, I had occasion to call once or twice on my namesake in Regent Street.

I do not pay postage in order to secure a more careful delivery.

With my respects to thyself and family, and to my few remaining friends at Eaglesfield, I remain,
thine sincerely,

JOHN DALTON.

P.S.—I shall remain two or three days here.

THE END

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